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**COLLISIONS OF THE SECOND KIND
THEIR ROLE IN PHYSICS AND CHEMISTRY**



PROFESSOR FRANCK

COLLISIONS OF THE SECOND KIND

THEIR ROLE IN PHYSICS AND CHEMISTRY

BY

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LONDON

EDWARD ARNOLD & CO.

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First published in 1937

Printed in Great Britain by
Butler & Tanner Ltd., Frome and London

PREFACE

This monograph may be regarded as a token of the author's interest—which he hopes will be shared by readers—in a concept which, although it has attained to its fullest value when expressed in terms of the quantum theory, really represents one of the latest flowerings of the perennially youthful classical thermodynamics. In one sense Professor E. K. Rideal, F.R.S., may be held responsible for this interest, which was engendered in 1925 by his suggestion that Professor Franck's recently stated general theory of collisions of the second kind, might with advantage be applied to observations upon the chemical properties of active nitrogen. In the twelve years which have elapsed since then, this generalized theory has been invoked to explain many phenomena whose origin would otherwise remain in obscurity, and it has accordingly appeared justifiable to publish this essay. It is a privilege to be permitted to pay homage to Professor Franck by inclusion of his portrait as frontispiece.

The author has throughout endeavoured to avoid two pitfalls, which may conveniently be described by allusion first to Sir Thomas Browne's dictum that "every man is not a fit champion for Truth, nor fit to take up the gauntlet in the cause of Verity"; and secondly, by the late Professor Bury's reference to the "disgusting vice of impartiality." It being, however, quite impossible for any single author to adopt a critical attitude upon topics ranging from spectroscopy to chain reactions, with *excursi* into thermionics and biology, a descriptive rather than a judicial style has been attempted, readers with authoritative knowledge being left, where differences of opinion are manifest, to form their own conclusions, with the assistance of the purposely extensive bibliography. The sections touching upon the sensitized plate and mitogenetic radiation are, frankly, only sketches, but are included as involving interesting subjects which are germane to the general plan of the book.

Notation, etc., is so far as possible in accordance with standard practice, but where spectroscopy is concerned the terminology of actual authors of papers has generally been followed, to assist in any reference back from this work to the originals. Any transcription which may be necessary can easily be effected by reference

to one of the standard works such as Dr. W. S. Jevons' "Report upon Band Spectra."

The author has made extensive use of valuable material extant in various earlier works. Especial reference may be made to the following :

Professor Franck and Dr. Jordan's "Anregung von Quantensprungen durch Stösse."

Drs. Griffith and McKeown's "Photochemical Processes in Gaseous and Liquid Systems."

Dr. Darrow's "Electrical Phenomena in Gases."

Professor Bonhoeffer and Dr. Harteck's "Grundlagen der Photochemie."

To a lesser extent, assistance has been derived from Drs. Mitchell and Zemansky's "Resonance Radiation and Excited Atoms" and Frl. Sponer's "Molekülespektren," both of which appeared when the manuscript was practically complete, and for part of Chapter VI, from Mr. Hinshelwood and Dr. Williamson's "Combination of Hydrogen and Oxygen."

The author's warmest thanks are due to many friends who have read sections of the manuscript and provided both suggestions and corrections. While full acknowledgment of all such services is impossible, his especial gratitude is due to Professor N. F. Mott, F.R.S., Dr. W. S. Jevons, Dr. M. L. E. Oliphant, Dr. H. W. Melville; and to Dr. W. H. J. Childs, Mr. J. A. Guy, Mr. K. Bridger, and other colleagues in this delightful Laboratory. But the principal salutations must be extended to Dr. H. C. Crouch, of St. Michael's, Ascot, and to Mr. G. Udney Yule, F.R.S., St. John's College, Cambridge, "men who sit in luminous silence and smoke pipes"; to the one, for restoration of health; and to the other—perhaps jointly with the first—for any wisdom and Johnian scholarship which their protégé may possess. To them, this little work is with all affection dedicated.

DAVY-FARADAY LABORATORY,
THE ROYAL INSTITUTION,
LONDON.

April, 1937.

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ACKNOWLEDGMENTS

The author's thanks are due for permission to reproduce diagrams which first appeared in the pages of the following Journals :

Proceedings of the Royal Society.

Philosophical Magazine.

Zeitschrift für Physik.

Zeitschrift für physikalische Chemie.

Journal of the American Acoustical Society.

Physical Review, and Reviews of Modern Physics.

Proceedings of the Cambridge Philosophical Society.

Annalen der Physik.

Physikalisches Zeitschrift.

ERRATA

Page Line

- v 18 For "fit" read "proper".
- 1 18 Delete reference 362.
- 3 1 Delete reference.
- 5 18 Delete reference.
- 5 20 For [9] read [8].
- 13 11 For [7] read [510].
- 13 41 Delete reference 46.
- 19 21 For "vary time" read "vary with time".
- 21 Footnote For "bond" read "band".
- 22 1 For [359] read "*Proc. roy. Soc.*, 1939, **123 A**, 168".
- For [360] read "*Z. Phys.*, 1934, **89**, 523".
- 24 22 For [360, 361] read [523].
- 24 41 For "— 0.96 V" read "— 1.96 V".
- 34 3 Delete reference.
- 34 10 Delete reference.
- 36 25 Delete reference 161.
- 40 13 Delete reference.
- 42 40 For [334, 335] read [335, 336].
- 43 16 For [336] read [337].
- 43 27 Delete reference.
- 52 5 For [304] read "*Proc. roy. Soc.*, 1934, **146 A**, 911".
- 74 Table 7 For "— Deactivation" read "% Deactivation".
- 75 Line 14 of footnote. Delete references.
- 76 26 Delete reference.
- 96 21 For "2P" read "3P".
- 101 8 For "Griffith and McKeown" read "Schumacher".
- 101 27 For "(O₂.O₂')" read "(O₂.O')".
- 103 19 For "formed" read "found".
- 112 2 For [488] read [458].
- 116 17 For "Williams" read "Williamson".
- 118 7 For "of nitrous oxide" read "of nitrous oxide [391—397]".
- 122 32 For "Knudsen" read "Knudsen [354]".
- 125 18 For "engendered" read "engendered [499]".
- 128 20 Delete reference.
- 128 21 For "Kirkby" read "Kirkby [509]".
- 129 21 For [511—518, 526] read [511—515, 526].
- 132 5 For "where the" read "where to the".

COLLISIONS OF THE SECOND KIND

CHAPTER I

INTRODUCTORY

Bohr's theory of the quantization of electronic orbits received its first experimental substantiation from the observations, originally due to Franck and his co-workers, and since repeated and extended by a host of other investigators, upon the loss of kinetic energy by controlled electrons directed into a gas or metallic vapour. In such a case, the projectile particles appear to traverse their path without any diminution of *vis viva* except when this equals the $h\nu$ value associated with a permitted electronic transition from the ground level to an upper excited state. For example, electrons passing through mercury vapour arrive at the collector with a velocity determined only by the accelerating voltage until this last reaches the critical value of 4.88 V, when the current-potential curve develops a very marked "kink" owing to the abstraction of kinetic energy from the electrons, and the vapour equally sharply commences to emit the mercury line at $\lambda = 2537 \text{ \AA}$. This type of collision has received much attention and the work, which is extant upon it, been admirably described by Franck and other authorities [279-282, ~~362~~], but much still remains to be done. In some cases—nitrogen for example—strong levels are known which do not reveal themselves towards a bombarding electron used in accordance with existing technique; in others, the form of the apparatus seems to influence the numerical values obtained for the energy levels under examination. As illustrations of fields yet to be explored we may mention the possible examination of the low vibrational states of molecules and their correlation with the "activated" levels familiar to physical chemists; and a further study of reactions induced by the impact of controlled electrons. Modern theory distinguishes between this type of impact—where kinetic energy is converted into the potential form—and the converse—

where potential energy is degraded in other ways—by the terms collision of the “first” and “second” kind respectively. They might, with much more justice, and considerably greater literary colour, be severally named after Franck and after Klein and Rosseland, but their general adoption into the vocabulary of science would suggest prudence as regards conventions, and we shall therefore follow the common usage as regards their application.

The probability of the existence of collisions of the second kind was first shown by Klein and Rosseland [1, 2] as a purely thermodynamic necessity and virtually independent of any quantum considerations. In a gas, free from electrons, but bathed in radiation corresponding to the temperature at which the gas is maintained, a statistical equilibrium between the molecules and radiation will obtain when the energy distribution in the latter conforms to the usual Planck condition. It would be expected that upon the introduction of electrons, this equilibrium would be disturbed, together with the appropriate distribution of velocities among the electrons for molecular excitation by electron impact, followed by radiation, would lead to a general decrease in the energy of the electrons, and an increase in that of the molecules and radiation, i.e. the apparent temperature of the radiation and molecules would rise and that of the electrons fall, so that the system would appear of itself to convey energy from a body at a low temperature to one at a higher, in transgression of the second law of thermodynamics. Hence it follows that a compensating influence must be applied, by the electrons themselves, which comes into action as soon as the new temperature equilibrium leads to a redistribution of their velocities, and Klein and Rosseland concluded that in an impact between an electron and an excited atom or molecule, the latter may undergo a radiationless transition from one quantum level to another, the energy set free going to raise the translational velocity of the electron concerned. The probability of such a collision is, moreover, equal to the likelihood of the loss of the same amount of kinetic energy by an electron in a collision of the first kind in order that thermodynamical equilibrium may be maintained in a mixture of atoms and electrons in which the Maxwellian distribution of velocities holds for both species [1, 2].

The full derivation of the principle proceeds as follows, the notation being that of the original authors. Consider an assemblage of atoms wherein n_1 are in energy level ϵ_1 , and n_2 in ϵ_2 , the statistical weightings of the two states being p_1 and p_2 . Einstein's

generalized form [322] of the Boltzmann distribution law then gives :

$$n_1 = Cp_1 e^{-\epsilon_1/kT} \quad n_2 = Cp_2 e^{-\epsilon_2/kT} \quad . \quad (1)$$

where k is Boltzmann's constant (i.e. the gas constant for a single molecule), T the absolute temperature, and C is a constant proportional to the total number of molecules present. Let now electrons be introduced whose energy distribution is Maxwellian in form, so that the number whose energies lie between ϵ and $\epsilon + d\epsilon$ is :

$$\mu(\epsilon)d\epsilon = K e^{-\epsilon/KT} \cdot \sqrt{\epsilon} \cdot d\epsilon \quad . \quad . \quad . \quad (2)$$

K being another constant independent of ϵ . Assuming then that the concentration of the atoms is so small compared with the electrons that the interaction of two of the former may be excluded, the probability of a collision of *the first kind* may then be defined by stating that the number of such impacts in unit time equals the product of this probability $S_{2-1}(\epsilon)$ with the number of atoms in the given stationary state and the number of electrons of the given energy. This is given by :

$$n_1 S_{2-1}(\epsilon) \mu(\epsilon) d\epsilon \quad . \quad . \quad . \quad (3)$$

and for the converse process (collision of the second kind) it is :

$$n_2 S_{1-2}(\epsilon) \mu(\epsilon) d\epsilon.$$

Now if $\epsilon < \epsilon_1 - \epsilon_2$, then $S_{2-1}(\epsilon) = 0$, i.e. the atom cannot be excited.

Considering further the equilibrium of electrons in the element $d\epsilon$ and lying between ϵ' and $\epsilon' + d\epsilon$, where $\epsilon' < \epsilon_2 - \epsilon_1$, we see that these can only undergo collisions of *the second kind* so that in unit time a number of electrons is lost equal to :

$$n_2 S_{1-2}(\epsilon') \mu(\epsilon') d\epsilon.$$

This must be compensated for by collisions of *the first kind* in the element between $\epsilon'' = \epsilon' - \epsilon_2 - \epsilon$ and $\epsilon'' + d\epsilon$, their number being :

$$n_1 S_{2-1}(\epsilon'') \mu(\epsilon'') d\epsilon$$

and the equilibrium condition for the element $d\epsilon$ between ϵ' and $\epsilon' + d\epsilon$ is given by :

$$n_2 \mu(\epsilon') S_{1-2}(\epsilon') = n_1 \mu(\epsilon'') S_{2-1}(\epsilon'')$$

which, since $\epsilon'' - \epsilon' = \epsilon_2 - \epsilon_1$, reduces with the aid of equations (1) and (2) to :

$$p_1 S_{2-1}(\epsilon'') \sqrt{\epsilon''} = p_2 S_{1-2}(\epsilon') \sqrt{\epsilon'} \quad . \quad . \quad . \quad (4)$$

This relation is excluded for the condition $\epsilon' < \epsilon_2 - \epsilon_1$, but it is

clear that it must be valid for $\epsilon' > \epsilon_2 - \epsilon_1$, because the collisions of the first kind for the element $\epsilon'' = \epsilon' + \epsilon_2 - \epsilon_1$, are compensated for by the reverse type of impact in the element ϵ' ; similarly, collisions of the second kind in ϵ'' are met by others of the first kind in $\epsilon''' = \epsilon'' + \epsilon_2 - \epsilon_1$, and so forth.

The principle derived above, as to the automatic balancing of collisions of the first kind by those of the second in order that thermodynamic equilibrium shall be maintained, may be termed Klein and Rosseland's principal postulate. It has, however, an important corollary. If we consider the form of equation (4) in conjunction with the well-established observation that the maximum probability of excitation of an atom by direct electron impact occurs when the electron energy exceeds the necessary value by only a very small amount [see 306-311], it follows that the energy of the latter body for the corresponding collision of the second kind should, to secure the greatest likelihood that *this* process will occur, be very small. Even on first principles alone, it would be expected that if two bodies are to interact, they will have the best chance to do so if they are moving relatively slowly with regard to each other and hence stay for some time within each other's range of attraction. This is Klein and Rosseland's subsidiary postulate, but, unlike the principal one, it has not so far been verified by direct experiment (see pp. 35 et seq.).

The concept of collisions of the second kind is, as pointed out by Saha and Sur [3], analogous with Einstein's "negative absorption"; in this, a Hertzian oscillator, placed in a field of radiation, will either emit or absorb energy according as the phase difference between the vibration and the field is less or greater than 90° . The physical principle from which it really derives is, however, that of "microscopic reversibility" or "detailed balancing," first definitely stated by Tolman [331] although, as he points out, others (Langmuir and Einstein for example) had tacitly adopted it some time before him. Its full derivation is beyond the scope of this book, and the reader may be referred to Tolman's original papers [331, and literature there cited] and to Fowler's later studies wherein the contributions of Dirac and others are considered [12].

In Tolman's words, it necessitates

that in a general way in the case of a system in thermodynamical equilibrium, not only that the total number of molecules leaving a given state in unit time shall on the average equal the number arriving in that state in unit time, but also that the number leaving by any particular path shall on the average be

equal to the number arriving by the reverse of that particular path, thus excluding any cyclical maintenance of the equilibrium state.

[See also 334.]

The Klein-Rosseland principle has been extended by Franck [6] and his school in one of the most important conclusions of recent years, to the generalization that it is equally valid for reactions between atom and atom as well as between atom and electron, and that there is a most complete interconvertibility of potential, radiational, and kinetic energy. Later work has shown that in collisions of the second kind the energy interchange may not of necessity be quantized so far as the acceptor goes, although the donor always loses its energy *per saltum* as in impacts of the first kind. Moreover, the most probable of all the possible modes of energy transfer are those in which (a) there is the least increase in the kinetic energy of the system, i.e. the maximum degree of quantization, and (b) there is no change in the total resultant spin momentum of the electrons of the participants. The first of these postulates, the so-called "resonance rule" is due to Franck [2a, 2b], and after further theoretical study by several authorities [9-13, 268] has been firmly established by Kallman and London [9] as a special case of quantum-mechanical resonance.

The second rule was derived by Wigner [15] from considerations of symmetry in electron configurations, but neither of these theorems will be discussed in detail at present since they can far better be illustrated in conjunction with the various experimental results by which they have been justified.

CHAPTER II

EXCITATION OF SPECTRA

When a mixture of the vapours of mercury and some other metal is illuminated by the resonance line of the first-named element at $\lambda = 2537 \text{ \AA}$, the latter may exhibit a very large part of its arc, or even part of its spark spectrum, through excitation in collisions of the second kind [16-19]. This is the so-called "sensitized fluorescence" of Franck and his school, and has been found of very extensive occurrence. The effects are frequently most vivid and

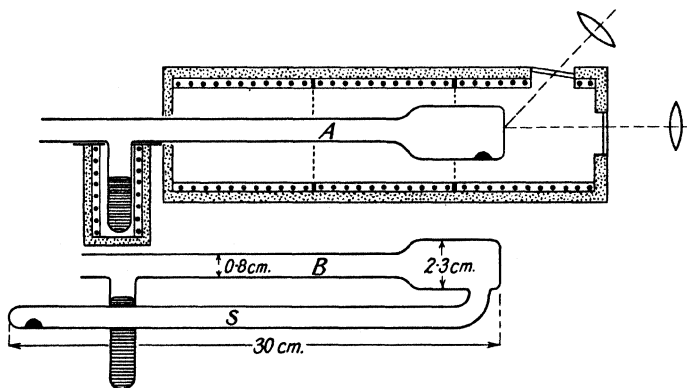


FIG. 1.—Apparatus for obtaining Sensitized Fluorescence of Metals (Loria).

beautiful, and easily demonstrable as a lecture experiment. Professor Franck's own illustrations of the sensitized thallium fluorescence will always be remembered by those who were privileged to see them. Technical details are to be found in Franck and Jordan's book [2] and in other papers quoted by Mitchell and Zemansky [256]. A simple example of the necessary apparatus is that used by Loria [120] (Fig. 1).

The metal to be examined is placed, in the form of a small pellet, at the wider end of the tube A, whose other end is connected to a pump. The side limb carries a small vessel containing mercury, and two electric furnaces are provided in order that the relative

vapour pressures of the mercury and the metal concerned may suitably be adjusted and controlled. The excitatory radiation enters through the lens which is aligned directly upon the tube A, while the fluorescent light is collected by the second lens near to the side window. By variations in the speed of pumping and the currents supplied to the heating coil of the furnaces, the desired conditions can soon be obtained. A modification suitable for use with metals of low boiling-point is shown in the lower figure, and needs no further explanation.

The many interesting phenomena arising out of this mode of energy transfer may now be considered in some detail.

Unquantized Liberation of part of the Energy of the Donor.

The following thallium lines have been observed in the fluorescence from a mixture of thallium and mercury vapours at 800° C. [7]:

TABLE 1

| Line. (Å) | Transition. | Excitation Potential. | Intensity. |
|-----------|-----------------|-----------------------|------------|
| 3776 | $2^2S - 2^2P_1$ | 3.3 Volts | S |
| 5350 | $2^2S - 2^2P_2$ | do. | S |
| 2768 | $3^2D - 2^2P_1$ | 4.5 Volts | W |
| 3529 | $3^2D - 2^2P_2$ | do. | VS |
| 2580 | $3^2S - 2^2P_1$ | 4.8 Volts | W |
| 3230 | $3^2S - 2^2P_2$ | do. | VS |
| 2826 | $4^2S - 3^2P_2$ | 5.3 Volts | W |
| 2920 | $4^2D - 3^2P_2$ | 5.2 Volts | W |
| 2709 | $5^2D - 3^2P_2$ | 5.5 Volts | VW |

S = Strong. VS = Very strong. W = Weak. VW = Very weak.

It will be noticed that the first two of these lines involves the emission of less than the energy (4.88 V) received from the optically excited mercury atom; hence the difference must be dissipated as kinetic energy. The last three, however, must necessitate participation of the *vis viva* of the atoms in order to provide for the deficit of nearly 1 V in the energies received and radiated. Although at 800° C. an appreciable fraction of the pairs of atoms will possess the 7000 and 9000 cal. required to bring the total energy up to that necessary for $\lambda = 2826$ and 2920 Å, only a small number will be able to furnish the 14,000 cal. for development of $\lambda = 2709$, and hence the intensity relations observed. The lines at $\lambda = 2768$ and

2580 Å are weak because they represent absorption lines of the normal thallium atom, and although the actual sensitized emission may be strong, the amount of radiation which emerges from the system will be small; this is not so noticeable for $\lambda = 5350$ Å, since although it is also one of the absorption lines it proceeds from an atom possessing high kinetic energy and hence giving a wide emission line due to Doppler broadening (q.v.): the centre only will be absorbed by the relatively slower unexcited thallium atoms, and hence the overall emission not be very much reduced.

It might be expected that when a collision of the second kind necessitates the liberation or absorption of kinetic energy, the emission line would be joined by a continuum extending towards the long or short wavelengths as the case may be [21, 22]. In fact, however, the region of diffuseness extends on *both* sides of the central line, and has a definite structure which for the part lying at the lower wavelengths appears to be due to a kind of Zeeman effect consequent upon the interaction of the magnetic moments of the outer electrons of the atoms, and for the other part to the setting-up of vibrational levels in unstable molecules formed upon collision of the excited atom with one of the diluent bodies. The effect has been observed by Krefft and Rompe [23] in a number of metallic spectra excited by a discharge in the presence of large amounts of a noble gas—where in the positive column bands due to unstable gas-metal compounds are very strong—and also by Oldenberg [24–26] in mercury-sensitized fluorescence phenomena. A discussion of the matter is given by Oldenberg and Kuhn [27].

Selective Development of Spectral Lines.

Addition of another gas to one whose spectrum is to be examined very often has a most remarkable effect upon the lines or bands developed. This is most pronounced with the noble gases as the diluents, and by a judicious selection of experimental conditions, the higher members of the atomic spectra, e.g. the spark and arc lines of the metals, and the arc lines of nitrogen and other gases which are hard to dissociate, may be obtained to the almost complete exclusion of continua and bands. Thus with condensed discharges through hydrogen in the presence of excess of helium at an overall pressure of ca. 30 mm., the intensity distribution of the hydrogen molecular spectrum completely alters; and if traces of carbonaceous bodies be added, the “Comet-Tail” bands of CO appear, although in the absence of the diluent they can only be obtained in very rarefied carbon monoxide [28, 29, 30].

Argon-hydrogen mixtures under the same conditions give a similar result although the effects are neither so pronounced nor even qualitatively the same [31]. Similarly, although the Merton-Johnson triplet series of CO bands may easily be obtained by means of condensed discharges in hydrocarbons mixed with a large excess of both helium or argon, with the latter gas neither the comet-tail bands nor a new line facies discovered by Merton [28] can be obtained under any conditions at all [32].

The Arc Spectrum of Nitrogen (N I).

Even more remarkable is the observation, due to Merton and Pilley [33] that the nitrogen arc lines, emitted by the neutral atom, may be obtained from helium at ca. 30 mm. pressure in the presence of a trace of nitrogen, a feeble uncondensed discharge being employed for excitation ; under these conditions, none of the spark lines (N II) due to N^+ , or the bands appears, but the effect cannot be reproduced with argon under the same circumstances. The action of the argon or helium was originally considered to favour the production of neutral atoms by reducing the electron speeds in the discharge ; since the resonance potentials of helium, for instance, are 19.7 and 20.4 V, whereas the most usual process of electronic dissociation of nitrogen is : $N_2 \rightarrow N + N^+$ at ca. 24 V, excitation of the helium would be favoured, at the expense of this mode of atom formation in nitrogen, especially in view of the somewhat high pressures concerned, which would tend to reduce the mean free path of the electrons and hence the energy which they would acquire between collisions with the gas molecules. But because a dissociation : $N_2 \rightarrow 2N$, the type to be expected from energy considerations for development of the N I series, would occur at less than 24 V, the helium would be beneficial through its action as discussed above, and, since under these conditions the partial pressure of the atomic nitrogen would be low, compared with the overall value for the mixture, recombination would be retarded. Hence while the helium would appear to act as a catalyst for the production of nitrogen atoms, and an anticatalyst for their destruction, argon would only behave in the latter capacity because its first resonance potential is so low (11.6 V) as to induce an excessive reduction in the electronic velocities.

Compton suggested, however, [34] that the dissociation here proceeds rather through collisions of the second kind between the excited helium atoms and the nitrogen molecules ; since the heat of dissociation of nitrogen was at that time taken to be ca. 19 V

[35], the reaction would not only be energetically possible, but of high probability, according to the resonance rule, since the two main resonance levels of helium fall at 19.7 and 20.5 V. The development of the N I lines would thus occur in two stages, viz. (a) $N_2 + He' \rightarrow 2N + He$, followed by : (b) $N + He' \rightarrow N' + He$, the N' then radiating away the energy acquired in process (b). It would seem that Compton's argument is substantially correct, although the much lower value now accepted for the heat of dissociation of nitrogen will render modifications necessary in the detailed mechanism of the reaction and, by reason of the large energy discrepancy involved, reduce the efficiency of the process (see pp. 25 et seq.).

The observed effects of rare gases upon a number of other diatomic gases are given in Table 2, which is derived, in the main, from Cameron's summary [36]; the lowest excitation potentials of the various systems have been added, and in Table 3 those of the noble gases used have been included for purposes of comparison.

TABLE 2

| System. | Emitter. | V | Helium. | Neon. | Argon. |
|--|------------------|---------|----------|---------|--------|
| Comet-tail bands . . | CO+ | 16.7 | S | s | A |
| Associated bands (Bal- det-Johnson) . . | CO+ | 19.8 | s | W | A |
| First negative carbon bands | CO+ | 19.8 | VS | s | VW |
| Swan bands . . . | C ₂ | No data | S | No data | s |
| Carbon arc lines . . | C | No data | s | A | A |
| Negative nitrogen bands | N ₂ + | 19.6 | S | S | A |
| Nitrogen arc lines (N I) | N | 11.7 | s | s | A |
| U.V. Oxygen bands . | O ₂ + | No data | W | W | A |
| Negative Oxygen bands | O ₂ + | No data | s | VW | A |
| Oxygen (O I) . . . | O | No data | s | s | s |
| Oxygen (O II) . . . | O+ | 13.6 | Doubtful | s | A |

In the above table, the following abbreviations have been used : S = Strong ; s = less strong, or not very noticeably present ; W = Weak ; VS = Very strong ; VW = Very weak ; A = absent.

The first four of the systems noted in this summary may all be obtained with carbon monoxide as the gas being excited in the presence of the diluent.

TABLE 3

| Gas. | Excitation Potentials. | Ionization Potential. |
|-------------------|------------------------|-----------------------|
| Helium | 19.77 20.55 | 24.5 |
| Neon | 16.58 16.77 | 21.5 |
| Argon | 11.57 11.77 | 15.7 |
| Krypton | 9.98 10.60 | 13.94 |
| Xenon | 8.39 9.52 | 12.08 |

The arc spectrum of nitrogen has more recently been extensively excited over the range $\lambda = 8800\text{--}3400 \text{ \AA}$ by a low voltage arc in a mixture of helium and nitrogen as used by Merton and Pilley, and Duffendack and Wolfe, to whom the experiments are due [38], adopt much the same scheme of reaction as did Compton. Secondary excitation of the atomic nitrogen by electron impact was not thought likely, since although the presence of the Negative Bands of N_2^+ upon the spectrograms indicated the existence of a considerable concentration of molecular nitrogen, the total amount of this element present made it impossible that more than 1 per cent of the electrons could have collided with nitrogen in any form whatever. Hence if the lines were developed in impacts of the first kind, their intensity, relative to the helium lines, should have been very small, in opposition to observation. Moreover, the Positive Bands due to neutral N_2 , have excitation potentials of the same order as the N I lines, and should also have appeared—unless, of course, they have a very different excitation-function [cf. 283] at the same time as the spectra originating from the atoms; but this again was not found to be the case. If then nitrogen molecules were to undergo collisions of the second kind with the excited helium atoms, the following sequence would be expected:

(a) The Negative Bands would be emitted in preference to the Positive series, since the energy discrepancy between the levels of the first named and that of the excited helium is less than one volt, whereas for the latter it is much greater (ca. 9–10 V); this follows from the resonance rule.

(b) The N I, rather than the N II lines, would appear on subsequent impact of neutral nitrogen atoms and helium, since not quite enough energy is available for stimulation of the spectra due to ionized atomic nitrogen. Similar experiments by More and Ander-

son [205] with argon-nitrogen mixtures show that the excitation here quite definitely occurs in two stages, the first being the dissociation of the nitrogen into one unexcited and one metastable $2D$ atom, followed by further stimulation of the latter, the source of the energy in each case being one or other of the metastable argon atoms with energies of 11.57 and 11.67 V; the high probability of the reactions, which would be expected from the resonance rule, is borne out by the appearance of the nitrogen lines with an intensity as great as that of the moderately strong argon lines, although the partial pressures of the gases ranged from 1 to 3 mm. Ar with 0.01 to 0.03 mm. N_2 .

Duffendack and Wolfe did not consider it likely that the nitrogen could be dissociated in a single act into one unexcited and one excited atom, the latter then radiating, since the lowest initial level of the N I series ($3p^4D_{\frac{1}{2}}$) has an excitation potential of 11.7 V, whence the minimum energy available would have to be 20.8 V, as compared with the maximum of 20.5 possessed by helium. Such a process does not, however, appear so improbable when we remember that the *metastable* helium atom of energy 19.8 V may be formed through neutralization of a fast ion at the electrode surface, very little kinetic energy being lost in the process of the ion is incident at a glancing angle upon the metal [155, 167].

Hence in the experiments under discussion, metastable atoms will be available having a total energy content of 19.8 V, plus a further amount extending up to the maximum kinetic energy acquired by the positive ions in the discharge, which would more than suffice for simultaneous dissociation and excitation of the nitrogen. The extent to which this occurs will naturally be dependent upon the conditions of working, together with other considerations arising out of the resonance rule and the conservation of spin momentum (q.v.). If the reaction were effected by rather fast helium atoms, so that the collision were partly of the first, and partly of the second kind, it might be anticipated that the resulting nitrogen atoms would possess a high kinetic energy and hence give a spectrum in which the lines would be somewhat diffuse owing to Doppler broadening, an inference which it would be of interest to examine experimentally. This particular case of selective development of one spectral series cannot as yet be regarded as satisfactorily interpreted, and further studies are needed, probably along the same lines as those made by Beutler and Josephy [40] and Beutler and Eisenschimmel [41, 62] (cf. pp. 25 et seq.). The observation that the N I lines may be

obtained in argon-nitrogen mixtures excited by a low-voltage arc [205] whereas they do not show up in a glow discharge under the same conditions [33], suggests that electrical effects should not entirely be ruled out as a source of some of the observations, and that the processes may be somewhat more complex than is at present supposed. Little assistance can be derived from experiments upon the excitation of the nitrogen spectrum by controlled electrons, since except for a few lines in the infra-red, due to N I [510] there seems to be an abrupt transition from the bands to the spark (N II) series, the intermediate stage, equivalent to the main arc spectrum, being absent [7]. It would appear that the molecular ion N_2^+ is formed at about 16–16.5 V, and that this in its excited state at 24 V undergoes either spontaneous or collisional dissociation into N and N^+ [37]. Evidence is, however, available that unexcited neutral atoms may be formed by collisions of the second kind in pure nitrogen excited by electron impact, since Lukirsky and Ptizyn have found [45] that at ca. 8 V the rate of the clean-up of the gas by magnesium undergoes a marked increase, probably through dissociation in a reaction between two metastable molecules in the $A^3\Sigma$ state, viz. : $2N_2(A^3\Sigma) \rightarrow N(2P) + N(2D)$, the metastable atoms then being absorbed by the metal to form a very stable nitride. This will be further discussed in connection with Cario and Kaplan's theory of the emission of the nitrogen afterglow (pp. 21 et seq.).

Recent studies upon the excitation potentials of the Second Positive Bands of nitrogen indicate that a combination of photoactivation and collisions of the second kind may be of much importance in some of these instances. In experiments similar to those of Lees and Skinner [241, 242] with a defined electron beam, spreading of the First, but not the Second Positive Bands outside the beam, was found [283]. This appears to be due to a primary excitation of the Lyman Bands, which upon absorption by neighbouring molecules raise these latter to the $a^1\pi$ level : here collisional transformation to the $B^3\pi$ state ensues with subsequent emission of the First Positive Bands in the $B^3\pi \rightarrow A^3\Sigma$ transition.

Similar results obtained upon the dissociation of hydrogen in the presence of argon, in a glow discharge, are easier to explain, since this latter gas has a resonance potential at 11.6 V, whereas increased clean-up, accompanied by some radiation, has been detected in the former under electron impact at 11.5 V, presumably due to formation of atoms [46, 250].

An excellent investigation of the effect in the metals has been made by Duffendack, Henshaw and Goyer [46], who excited the Mg II spectrum in a low voltage arc at ca. 1000° C. in the presence of hydrogen, argon, neon, and helium. As is often the case with spectra obtained through collisions of the second kind, the intensity distribution was quite different from that given by electron impact, but the level of the excited magnesium ion never exceeded, by more than a few tenths of a volt, that of a corresponding metastable or ionized state of the gas molecule. (For discussions as to the origin of these abnormal intensity distributions see McLennan, Ruedy and Anderson [47].) That the lines obtained here necessitate the occasional participation of the diluent gas the ion, is an illustration of the very important principles of ionization by electron transfer, which will be more fully studied later on; such a reaction may be represented by: $\text{Mg} + \text{Ar}^+ \rightarrow \text{Mg}^{+'} + \text{Ar}$. Moreover, the appearance of lines whose excitation potentials are greater than that of the gas molecule or ion concerned, shows that the kinetic energies of the impacting bodies must in some instances be drawn upon for the conversion into the internal form. This is exemplified by the development of the $8f^2F$ level by the ionized neon; here V_i for neon is 24.5 V, whereas V_e for the state concerned is 24.73 V, leaving a discrepancy of 0.23 V to be contributed from the *vis viva*, which in a gas at 1000° C. would certainly be available. (The fraction of molecules having energies greater than 0.23 V is ca. 0.14 under these conditions.)

Collisions of the second kind are considered by Duffendack and his associates to be particularly effective in the development of spectra in hollow cathodes when an ordinary glow discharge is passing between the poles of the metals under examination in the presence of one of the noble gases, a method first employed by Paschen [219]. Under these circumstances, the spark lines of gallium and indium are excited to the levels which could be reached by impacts of the second kind with metastable atoms or ions of helium [48], while with cadmium under the same conditions definite intensity maxima would appear, corresponding closely to the maximum excitation and ionization potentials of the diluent gas [49].

The process may, however, be rather more complicated, metallic ions first being formed by some other mechanism, and then excited, as a rule by metastable atoms of helium; but in the positive column, the neutral atoms are the most usually affected [50]. The problem has been investigated by Sawyer [218], and it appears that in general

the metal is excited to a term in its spark spectrum with gain or loss of only a very small amount of kinetic energy to balance out the reaction equation. In view of the very involved nature of even the simplest glow discharge, it would appear somewhat difficult to formulate any general rules upon such matters, since the results will be so susceptible to the conditions of experiment, and more data are essential before anything more than very cautious suggestions can be made [51] (cf. also 147).

The "Enhancement" Effect.

The development of metallic spectra has more recently been studied semi-quantitatively by Duffendack and Thomson [52] who have examined certain line groups of silver, copper, aluminium, and gold, all derived from a common upper level, as they are excited (a) in the normal arc with the addition of neon or helium, and (b) in the condensed spark in the absence of any noble gas, the numerical ratio of the intensity in condition (a) to that in condition (b) being termed the *enhancement* and taken as a measure of the efficiency of the collisions of the second kind to which their appearance in the first case is due. The results for copper spark lines excited by ionized neon are given in Table 4, and show that the less the energy discrepancy between the states concerned, the greater, as a general rule, is the enhancement. Here I_{Ne} and I_n are respectively the intensities with and without neon, ΔE is the energy discrepancy, in volts, between the level of the ionized neon and the common upper state of the excited copper atom, and the average value is that of the enhancement I_{Ne}/I_n . Very similar results were obtained with silver and the other metals used, but in all cases it appeared that the *type* of level being excited is of much importance in determining the magnitude of the enhancement. For copper, for example, the plot of I_{Ne}/I_n against ΔE gives a smooth curve for the triplet levels, but the point for the singlet levels does not fall upon the graph since its enhancement is only 9.7 as compared with the 18.5 demanded were it to be concordant with the first-named data. The effect is not that predicted by Wigner's rule (q.v.) although it does to a certain extent resemble it, and, since these experiments show the existence of another factor as regards the enhancement, apart from any questions of energy-resonance, it is to be hoped that further studies along these lines will, in due course, be made. (Other examples of spectra excited in this manner are given in references 51, 52-55, and 206.) In the latest studies upon such excitation processes, due to Manley and Duffendack [286] attempts have been

TABLE 4

| Line. | Initial Level. | I_n . | I_{Ne} . | I_{Ne}/I_n . | $\Delta E(\text{Volts})$. |
|---------------|----------------|---------|------------|----------------|----------------------------|
| 2527 | $(d^9s)^3D_3$ | 2.2 | 2.2 | 1.0 | 0.40 |
| 2545 | | 10.0 | 10.0 | 1.0 | |
| 2689 | | 4.7 | 4.7 | 1.0 | |
| Average . . . | | | | 1.0 | |
| 2506 | $(d^9s)^3D_2$ | 6.9 | 19.7 | 2.8 | 0.36 |
| 2599 | | 2.8 | 7.4 | 2.6 | |
| 2666 | | 1.8 | 4.4 | 2.6 | |
| 2714 | | 4.7 | 13.3 | 2.8 | |
| Average . . . | | | | 2.7 | |
| 2486 | $(d^9s)^3D_1$ | 4.3 | 57.0 | 13.2 | 0.16 |
| 2591 | | 2.1 | 32.0 | 15.2 | |
| 2703 | | 3.8 | 57.0 | 15.0 | |
| 2722 | | 1.9 | 27.0 | 14.7 | |
| Average . . . | | | | 14.6 | |
| 2529 | $(d^9s)^1D_2$ | 4.2 | 40.0 | 9.5 | 0.12 |
| 2600 | | 4.4 | 44.0 | 10.0 | |
| 2701 | | 4.8 | 48.0 | 10.0 | |
| 2719 | | 3.8 | 35.0 | 9.2 | |
| Average . . . | | | | 9.7 | |

made to measure the effective cross-sections for impact in the system magnesium-ionized neon as a function of the energy discrepancy for various states. Conditions were chosen to enable accurate spectrographic estimations to be made upon the "population" of these states first by direct electronic excitation and then through collisions of the second kind between the magnesium and neon ions, the ratio of the latter to the former values being taken as a more precise "enhancement" than in the earlier investigations [46, 52]. The arc line $4^3D \rightarrow 3^3P_2$ at $\lambda = 3096 \text{ \AA}$ was used as the reference standard in order to reduce possible errors from direct electronic development of the spark lines being studied, although tests showed that these are but little excited by ordinary kinetic impact.

The logarithmic plot of intensity of a number of the Mg II lines against pressure of neon, is given in Fig. 2, taken from Manley and Duffendack's paper. It appears that the excitation of the lower members is mainly electronic—since they are but little affected by neon pressure—but that the higher terms originate in

collisions of the second kind with the gas ions. As the authors point out, the possibility must not be neglected that some of the levels may be developed by transitions from higher states, but since the number of such transitions would be proportional to the cube of the frequency concerned—here a line in the infra-red—the probability of such a process would be small compared with the mechanism under consideration. The form of the curves for the enhancement plotted against ΔE differs somewhat from those to be expected from Kallmann and London's equation for energy transfer as a function of the energy discrepancy [8] which, for the adiabatic

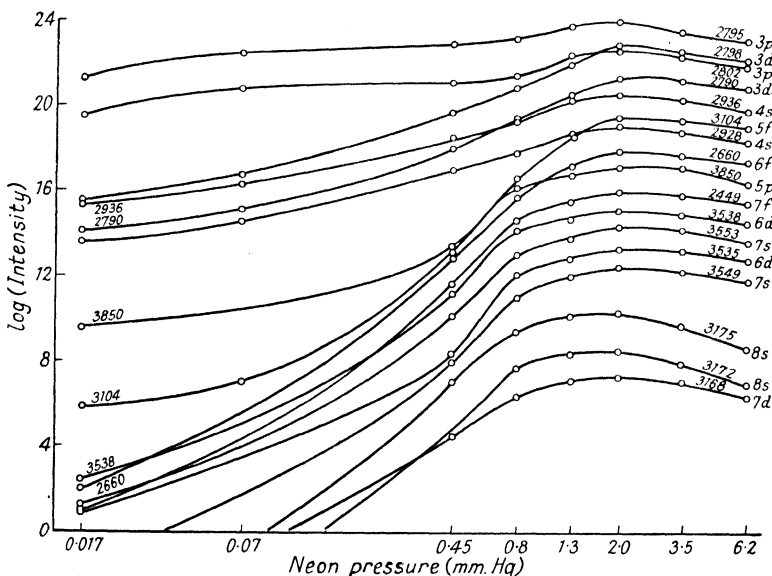
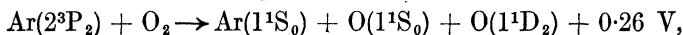


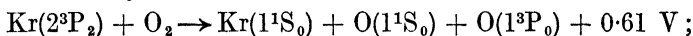
FIG. 2.—Effect of Neon upon Magnesium Spark Lines (Manley and Duffendack).

process dealt with, demands an infinitely large value of the cross-section when $\Delta E = 0$ (see p. 44 et seq.). Here, as in Kallmann and Rosen's actual experiments [137] the prediction is not fulfilled—as is only to be expected in view of the approximations introduced—and Manley and Duffendack calculate a cross-section some 10^5 times that of the "kinetic" value, in agreement with estimates made by Stueckelberg [287] on the basis of quite reasonable interaction potentials. It does not as yet seem possible to explain why the enhancement appears to depend upon the nature of the terms concerned, Manley and Duffendack's own explanation being somewhat unconvincing.

Another example of even more accurate quantitative work through the application of this principle is Witmer's study of the Lyman bands of hydrogen, obtained by admixture of this gas with argon in a glow discharge; so much of the series was obtained that only a very short extrapolation was necessary for the determination of the convergence limit—and hence the heat of dissociation of hydrogen—to a high degree of accuracy [56]. The detailed mechanism of the process has been established by Beutler [250, 329]. A mixture of hydrogen and neon, under the same conditions, gives a Balmer spectrum which is very strong in the higher members, while the neon loses its ability to absorb those lines which are derived from the 2^3P_2 metastable level [57–61]. This must mean that dissociation of the former gas is proceeding, clearly through collisions of the second kind, and Beutler and Eisenschimmel [62] suggest as the mechanism: $Ne' + H_2 \rightarrow Ne + H(3^2P) + H + 0.13 \text{ V}$. This implies an enhancement of $H\alpha$ with respect to $H\beta$ and $H\gamma$, which is observed in this case, but not when the dissociation is affected through the action of excited or metastable helium atoms. It moreover involves the formation of atoms of kinetic energy ca. 0.06 V each and hence a Doppler broadening of their emission lines such as would be given by bodies in a gas at 430°C .; a grating spectrogram taken with the discharge tube immersed in liquid air, showed such a widening of the magnitude calculated. The appearance of the green auroral line at $\lambda = 5577 \text{ \AA}$ in mixtures of oxygen with argon or krypton, noticed by McLennan and Ireton [63], may be due to the dissociation of the first-named gas into one or more metastable atoms in a sequence such as:



or alternatively,



the line is then radiated in a transition from the metastable 1^1S_0 state to the other metastable 1^1D_2 level. The main auroral spectrum, however, originates in a much more complicated process, and it does not as yet seem possible to explain the reactions involved although indications have been obtained that it may represent a superposition of discharge and afterglow spectra in which the metastable $A^3\Sigma$ state in nitrogen plays an important part [64, 65].

Active Nitrogen.

The spectrum of the nitrogen afterglow represents an extremely interesting example of selective development of a band series in

collisions of the second kind. When nitrogen of not too high a degree of purity is drawn at pressure up to ca. 10 mm. through a condensed discharge, it exhibits a very beautiful yellow luminosity which persists for some time as the gas flows towards the pump; in static systems, where the glow can be excited by an electrodeless discharge at lower pressures (0.1 mm. and less), its duration may extend up to thirty minutes although the light is then very feeble [66, 67, 251]. (Rayleigh, using a large bulb whose walls were rendered catalytically inactive by treatment with metaphosphoric acid, a substance found by von Wartenberg [362] to be extremely effective in preventing the wall recombination of hydrogen atoms, has recently observed the glow five hours after excitation [360].) At the same time, the nitrogen becomes abnormally reactive, and can combine with many substances towards which it is usually quite inert. It was at first supposed by Strutt (now Lord Rayleigh), to whose classical investigations [67] the greater part of our knowledge of this "active nitrogen" is due, that the luminosity merely represents the emission of the heat of recombination of two atoms in a bimolecular reaction; the decay of the afterglow should therefore be a second-order process with respect to the glow-producing bodies and its intensity I vary time t according to the equation: $I/\sqrt{I} = At$, A being a constant; this has been verified in several investigations [68-74]. Since Fowler and Strutt had found [75] that the banded spectrum of the afterglow consists merely of a selection of the First Positive group of nitrogen, due to N_2 , save for a greatly enhanced intensity of the bands in the red, yellow, and green, Frl. Sponer [76] suggested that the luminosity arises from a chemiluminescent recombination of two atoms in the presence of a molecule, this last being excited in the process and then radiating as in the parallel case of metallic spectra developed through the termolecular reaction: $2H + M \rightarrow H_2 + M'$ [86]. The maximum energy associated with the afterglow spectrum (at that time taken as ca. 11.5 V) agreed well with the heat of dissociation then accepted for nitrogen, this latter value being derived from the extrapolated convergence limit of the vibrational sub-levels of the normal X state of N_2 , by the use of data from the Birge-Hopfield "ultra-violet" band [77]. (For a discussion of this method for the determination of heats of dissociation, see Jevons [363].)

Willey [71, 72] also concluded that the glow-emission process is termolecular, since Strutt had observed that the intensity of the luminosity is enhanced at the expense of its duration either by

compression or cooling of the glowing gas, as would be expected from considerations upon the chemical kinetics of such a reaction. It has, moreover, been shown that the influence of pressure is quantitatively in accord with this view, provided that complicating surface effects are excluded [70, 74, 361], but the simple theory can no longer be maintained since it is now recognized that part of the afterglow bands originate in states having far too much energy to be furnished by the heat of association of the atoms [78, 79, 252].

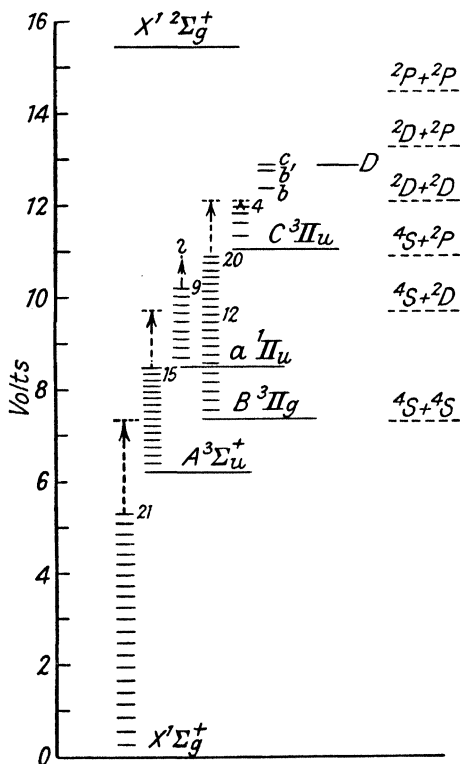
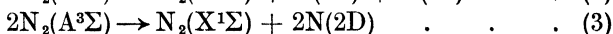
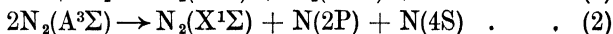
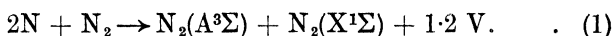


FIG. 3.—Energy Levels of the Nitrogen Molecule (Cario).

In the condensed discharges used for the preparation of active nitrogen, there is a strong development of the Fourth Positive Bands, for which the upper electronic state has only the $v' = 0$ level. Kaplan has supposed this to mean either that the vibrational states converge immediately above, so that D for the molecule in this condition must be small; or alternatively, that it may be due to the perturbation of this upper state by another whose poten-

tial energy curve intersects that of the first at or close to $v' = 1$ [80]. (Pre-dissociation would seem a much more likely reason for this absence of vibrational levels of the $D^3\Sigma$ state.) The molecule in this condition will thus be very unstable, and dissociate adiabatically into two metastable atoms, i.e. : $N_2(D^3\Sigma) \rightarrow N(2D) + N(2P)$, the energies of the 2D and 2P states being 2.37 and 3.56 V respectively [81]. Now the lower state of the First Positive Bands, the $A^3\Sigma^+u$ level is metastable since transitions from here to the ground level $X^1\Sigma^+g$, although known,* are weak because of the multiplicity change involved, and hence we should expect—since the First Positive Bands are also strong in the discharge spectrum—that in active nitrogen a mixture of these three metastable species will be present, together with neutral unexcited atoms formed through dissociation of the excited molecular ion (cf. p. 12). These considerations have been used by Cario and Kaplan [82] to explain the emission of the afterglow by a theory which, although more complex than the earlier ones, does provide for a number of phenomena which could not previously be accounted for. While recognizing that the ready dissociation of the $D^3\Sigma$ state may provide *some* of the 2D and 2P atoms present, they suppose that these may also be formed in the reactions :



(The small energy discrepancies in reactions 2 and 3 clearly render them quite probable.) The afterglow bands then follow from collisions of the second kind between the metastable atoms of both species, and the metastable molecules.

Those of the latter in vibrational states of level A are excited to vibrational levels of state B, these being given by $v' = 10, 11$ and 12 for excitation by $N(2P)$ and $v' = 6$ and 7 where $N(2D)$ is concerned ; the energies here are 9.70 and 8.51 V respectively. Transitions from these B levels to states $v'' = 7, 8$ and 9 and $v'' = 3$ and 4 of level A then occur, with the emission of the peculiar selection of the First Positive Bands which comprise the afterglow ; of these, the process :

$B(v' = 10, 11, 12) \rightarrow A(v' = 7, 8, 9)$ gives the α -bands, while the other :

$B(v' = 6, 7) \rightarrow A(v' = 3, 4)$ gives the infra-red series, studied

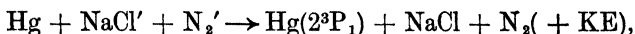
* The Vegard-Kaplan intercombination bond ; cf. 521-3.

particularly by Kichlu and Acharya [359] and Cario [360]. Considered from the energetics standpoint alone, the latter band may also be developed in a termolecular reaction between $N_2(A^3\Sigma)$, $N(4S)$ and $N(2D)$ [see 85].

The theory has been criticized by Okubo and Hamada [83], but it would appear amply justified since, for example, it also explains both the electrical conductivity of the afterglow and the effects of temperature and pressure upon the luminosity. The former appears to be due to the emission of electrons consequent upon deactivation of the metastable molecules at the surfaces of the testing electrodes [84] as in Oliphant's experiments with metastable helium atoms [155] while the latter follow from the termolecular process of formation of these same bodies [cf. 361].

Since we have here a chain reaction, in which the overall velocity will be determined by the speed of the slowest step, i.e. No. 1 of the above processes, the glow-emission will be bimolecular with respect to the primary active species—the atoms N —but of the third order when the pressure is taken into account. Steps (3) and (4) might account for the observation by Lukirsky and Ptizyn [45] that the clean-up of nitrogen by magnesium when the gas is acted on by slow electrons commences at 8 V; some formation of metastable molecules might be expected at about this point,* but the possibility must not be overlooked that the effect might also be due to some type of cumulative excitation leading to dissociation in another manner.

Cases are in fact known where collisions of the second kind occur among excited bodies of the same species, leading to the development of spectra which could not be obtained were the energy of only one of the participants available. When sodium vapour reacts with chlorine in the presence of large excess of nitrogen and a trace of mercury at atmospheric pressure, the line $\lambda = 2537 \text{ \AA}$ may be observed [319], this being due, according to Beutler and Josephy [320], to the termolecular process:



$NaCl'$ being a nascent sodium chloride molecule holding its heat of formation from its elements (4.06 V) while N_2' is a molecule in possession of sufficient vibrational energy—derived from collision with other $NaCl'$ bodies—to effect an energy balance. Mercury lines of

* Or possibly even some dissociation, in view of the value now accepted for the heat of dissociation of nitrogen.

the 3^3D_n series may also be developed under the same conditions—except for the absence of nitrogen [320]—the only reasonable mechanism being a bimolecular impact between one 2^3P_0 and one 2^3P_1 atom. Since the 4.06 V available from the NaCl' is insufficient to excite even the 2^3P_0 mercury state, it follows that *four* nascent sodium chloride molecules must have been involved, one pair to each of the mercury atoms concerned. Wood has also observed the appearance of $\lambda = 2856 \text{ \AA}$ in mercury vapour exposed to $\lambda = 2537 \text{ \AA}$ in the presence of nitrogen [321], a process which seems to be due to the impact of two 2^3P_0 atoms wherein *one* receives the whole of the energy [323]; this is very probable on the basis of the resonance rule, since the level from which $\lambda = 2856 \text{ \AA}$ originates (3^1S_0) lies only 0.11 V below that equivalent to $2 \times 4.68 \text{ V} = 9.36 \text{ V}$, so that the kinetic energy to be dissipated is merely that associated with a pair of atoms at 380°C . (Numerous examples of this kind of reaction, with bibliographies, are given in papers by Beutler and his collaborators; see especially 62, 320, 325, 328: others are 40, 41, 131, 320–324, 326–329.)

Evaluation of Heats of Dissociation, etc.

If the recombination of two atoms A takes place in a termolecular reaction with a third atom or molecule B with spectral excitation of the latter, an inferior limit to the heat of dissociation of the molecule A_2 can clearly be obtained from an examination of the spectra emitted by B in the process. Magnificent luminous effects often appear when metallic vapours are introduced to a stream of atomic hydrogen or active nitrogen, and the principle just mentioned has been used with some success to determine D for H_2^* . Such experiments with atomic hydrogen led Bonhoeffer [86] and Mohler [87] to place the upper limit to the heat of dissociation of hydrogen at

* Particularly beautiful colours appear if iodine or bromine be added to active nitrogen, and may easily be shown as a lecture experiment provided that a pump of large capacity be available. The active nitrogen should be drawn through a large vessel (e.g. a 20-litre gasholder) which is fitted with a side tube so that just before the main gas enters the reservoir it can be dosed with a tributary of unsparked, oxygen-free hydrogen, containing a trace of the halogen. Adjustment of the quantity of iodine or bromine may conveniently be made by allowing it to diffuse into the hydrogen from a side tube which is initially cooled to ca. -80°C . but allowed to warm up somewhat when once a strong afterglow has been obtained. With bromine, the glow becomes a vivid crimson which, when the refrigerant is replaced, runs through a magnificent series of reds and purples until finally the original yellow reappears. Iodine gives a blue luminosity, and as it is cut off gives rise to a sequence of colours comparable only with an Alpine sunset.

87,000 to 100,000 cal./gr. mol., and Kaplan [88] has more recently found that the less the energy carried away by the resulting hydrogen molecule in one of its known vibrational levels, the greater is the intensity of the metallic level thus excited; this appears to be a particular case of the "resonance rule" mentioned earlier.

Bay and Steiner [89] vaporized mercury into a stream of luminous active nitrogen and found that while the 4^3D triplet system ($V_e = 9.5$ V) was strongly excited, the 5^3D series (9.8 V) did not appear, whence it follows that if the mechanism involved is: $2N + Hg \rightarrow N_2 + Hg'$, $Hg' \rightarrow Hg + h\nu$, the heat of dissociation $N_2 \rightarrow 2N$ must lie between 9.5 and 9.8 V. The luminescence here was of considerable duration, but when 15 per cent H_2 was added to the nitrogen before sparking both the normal nitrogen afterglow and the lifetime of the mercury emission were much diminished, the latter also exhibiting a different intensity distribution as compared with the parallel case where the hydrogen was absent. Under these conditions, the mercury excitation ceased with the 2^3S term (7.7 V +), the next highest ($3^3D = 8.7$ V) not being seen, and it thus appeared that the stimulation is here effected by the metastable nitrogen molecule ($A^3\Sigma$). It would, however, seem that some other explanation of these observations must now be sought, since D is known to be 7.34 V [360, 361] and the direct electronic evaluation of the energies of the mercury states concerned admits of no doubt as to their accuracy. The very complex nature of the gas mixture, with its variety of metastable species of both nitrogen and mercury, clearly renders the task of alternative suggestions a very difficult one.

The low value now accepted for D in nitrogen also explains the failure of McLennan, Reudy and Anderson [47] to excite the 8.3 V metastable state in xenon by means of active nitrogen; the excitation potential is here 0.96 V *above* that of the metastable $N_2(A^3\Sigma)$, and the alternative mechanism: $2N + Xe \rightarrow N_2 + Xe' - 0.96$ V, is unlikely to be operative because of the large amount of kinetic energy required to effect an energy balance. A small effect might, however, have been anticipated through a reaction between Xe, $N(2D)$ and $N_2(A^3\Sigma)$. (This paper contains a number of very interesting spectrograms relating to active nitrogen.) It may be mentioned that evidence is not lacking that in some cases, these spectra may merely represent chemiluminescence attendant upon the formation of highly exothermic compounds such as nitrides and oxides. As is pointed out elsewhere (p. 60 et seq.), the heat liberated in these chemical reactions may give rise to various phenomena for which

purely physical explanations have been devised, and caution is therefore essential under such circumstances (cf. 190 and references there cited).

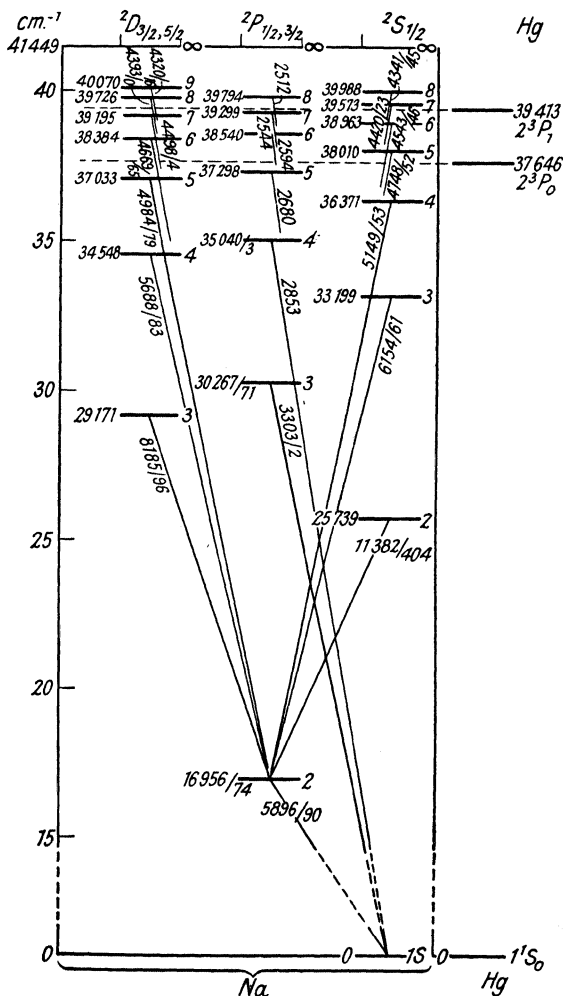


FIG. 4 (a).—Energy Levels of Na and Hg (Beutler and Josephy).

The "Resonance Rule."

A number of attempts have been made to verify this rule quantitatively by study of the intensity of various spectral lines excited in collisions of the second kind, but the results do not appear to be very dependable because of the rather complicated experimental condi-

tions so often employed and the inadequate photometric technique used in measuring up the plates. It has, however, been examined very elegantly by Beutler and Josephy [40] for the mercury-sensitized fluorescence of sodium, this latter metal being particularly suitable by reason of its numerous levels in the vicinity of the two 2^3P_1 and 2^3P_0 states of the photo-excited atoms concerned (Fig. 4). Their investigation showed, after the application of various corrections for statistical weighting of the level involved and the changing response of the plates to different wavelengths, etc., that the maximum intensity of the fluorescence spectrum occurred at

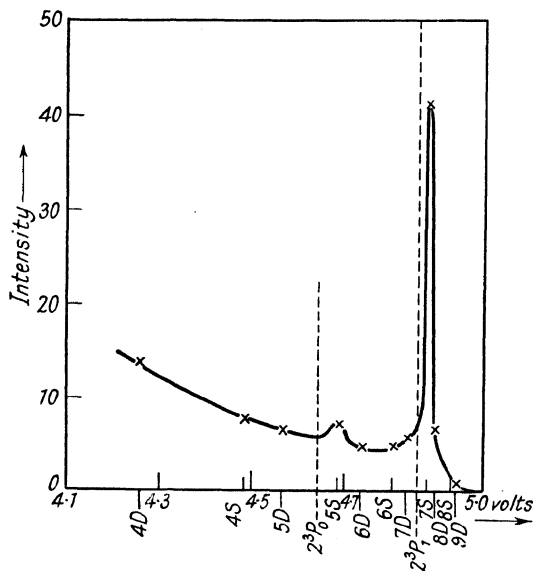


FIG. 4 (b).—Spectral Region (Beutler and Josephy).

$\lambda = 4423 \text{ \AA}$, and hence at a level whose excitation potential lies at 0.02 V *vis-à-vis* that of the 2^3P_1 mercury state. Addition of 0.97 mm. of nitrogen developed a second maximum at $\lambda = 2594 \text{ \AA}$, owing to resonance between this level and the metastable 2^3P_0 mercury state, the latter being derived from the higher 2^3P_1 atom by collisional degradation of the 0.218 V difference between them. An even more marked effect should have been found for the sodium line $\lambda = 2544 \text{ \AA}$, but it could not be studied quantitatively because of the halation induced upon the photographic plates by the very intense mercury line at $\lambda = 2537 \text{ \AA}$. (An ingenious method of avoiding this difficulty has been described by Oldenberg and Kuhn

[27]; another tube containing pure mercury vapour is interposed between the reaction vessel and the spectrograph so that the resonance line is largely absorbed, although lines due to other elements are transmitted unaltered.)

Wigner's Rule.

As originally stated [15], this principle postulated that if a collision of the second kind may, from the standpoint of energetics alone, occur in several ways, the most probable of all of these will be that for which the multiplicity of the whole system remains unchanged. Hence if in one of the bodies concerned a triplet-singlet intercombination occurs, and the energy conditions permit of a similar intercombination in the other, then *two* intercombinations will take place simultaneously in preference to *one* which is accompanied by a permitted transition in the second atom or molecule involved. In other words, the total resultant spin momentum S must remain constant, since by definition the multiplicity equals $(2s + 1)$, s being the resultant spin of all of the electrons in a given state. A physical picture of the effect demanded may be derived from Fig. 5, in which the arrows represent the spin vectors of the electrons in the triplet and singlet systems.

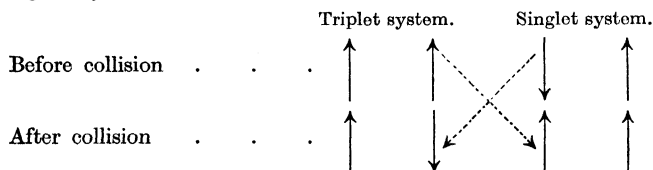
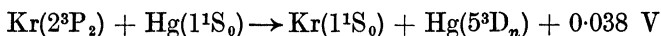


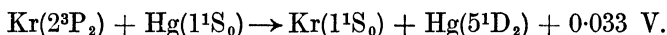
FIG. 5.

The two systems have interchanged electrons, but in such a manner that the triplet system has become a singlet at the same time as the singlet has changed to a triplet, so that the overall multiplicity is the same after collision as before. It will be noticed that the theorem closely resembles the familiar selection rule of spectroscopy, whereby a triplet-singlet intercombination will occur either not at all or with very considerable reluctance. Hence where the multiplet splitting is high, the principle may not necessarily be obeyed, as will be seen later. Moreover, in the rule as originally stated, Wigner neglected possible coupling effects between orbital and spin momentum, but evidence is not yet available as to how far this is justifiable [cf. 241, 242]. The two 5^3D_n and 5^1D_2 terms of mercury are in very close resonance with the 2^3P_2 level of the krypton atom, and it would be expected that from the standpoint

of energetics and the resonance rule alone they would be equally developed in a collision of the second kind. An investigation by Beutler and Eisenschimmell [41], in which the mercury lines were photographed in a discharge in the presence of krypton and helium or neon, showed however that the process :



is some thirty times as likely as the other possible reaction :



In the first case, where the triplets are excited, the value of S remains unchanged at unity ; but in the second, where the singlets appear, S has now fallen to zero.

A similar effect was also observed when the excitation was carried out by the 2^3P_1 krypton atom to give the 6^3D_n and 6^1D_2 states in the mercury with energy discrepancies of only 0.019 and 0.017 V respectively, but here the factor of probability is only ca. 3. There may be some analogy, although not as great as Beutler and Eisenschimmell suggest, between these reactions and the corresponding excitations of the singlet and triplet systems of mercury by electron impact. Investigations by Schaffernicht [91] and Foard [92] have shown that the probability of excitation of the former, plotted against the accelerating voltage, shows a gradual rise to a broad maximum at ca. 50 V, whereas the same curve for the latter rises much more steeply to a narrow maximum just above the calculated critical potential and then rapidly falls away. Since the development of the triplets may be regarded as involving the interchange of a free and bound electron with anti-parallel spins, the multiplicity remains constant, and the probability of the reaction occurring will accordingly be high, according to Wigner's rule, when there is a good resonance between the systems. With the singlets, the multiplicity changes, and hence the process can take place when the resonance is less sharp.

This electron interchange may become of considerable importance when molecular collisions are concerned, since the effective duration of the impact is then comparable with the period of vibration of the molecule. Under these conditions, the inner electrons are also affected [93], leading, as in the case of a hydrogen molecule in contact with a 2^3P_0 mercury atom, to the inception of a state comparable with that obtaining when considerable thermal energy is available and hence to a dissociation of the hydrogen. This implies the existence of an important time factor in excitation processes

such as that considered above, and it is of interest that when the metastable 2^3P_2 krypton atom is concerned, the Wigner effect is ten times as pronounced as in the other case when the short-lived 2^3P_1 atom is the source of the energy transferred, which suggests that in the latter reaction one of the bodies involved changes its nature before its work is ended.

Excitation of the helium triplet and singlet systems by electron impact appears to offer a better suggestion as to the application of Wigner's rule in such cases. Calculations show that to excite a triplet state, an incident electron must collide almost head-on with an atomic electron with anti-parallel spin, so that the latter is ejected and the former left with just enough energy to give the excited state. The probability of this decreases inversely as the square of the energy of the bombarding electron. On the other hand, to excite the singlet state the electron need impart only a small fraction of its energy to the atomic electron, which when high energies are involved, is not so unlikely an occurrence; moreover, there is no need for the electrons to change places.

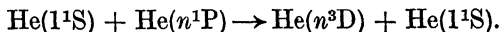
In a recent discussion of the problem, Wigner and his associates point out that the conservation principles of quantum mechanics fall into two groups [237]. The first comprises the energy and the momentum rules for both head-on and glancing impacts, the last-named circumstances not being determinable by means of collision effects. The limits of validity for these rules cannot as yet be indicated either by quantum mechanics, or by the classical methods. The second group consists of the original postulate as to the conservation of electron spin momentum (which includes, of course, the total proton spin as well). The latter group, with which we are here concerned, has been verified both in cases (a) where there is close resonance and also (b) where kinetic energy has to be drawn upon to effect an energy balance. As examples of method (a) we have the numerous experiments upon para-hydrogen, which show that this substance has a marked reluctance to pass into the ortho-modification with a different value of S [see 238],* the investigations of Wood and Loomis upon iodine fluorescence [239] and the elegant studies of Beutler and Eisenschimmell upon the excitation of mercury lines by excited krypton atoms [62, 240], although the last named have confirmed the Wigner principle only in its statistical aspects.

* It would be expected that Wigner's rule would here be strongly operative, in view of the rigidity of the selection principle for nuclear transitions.

In the case where the kinetic energy of the other partner of the impact influences the deactivation energy of the first atom, theory does not indicate any differences from the preceding one as regards the validity of the rule. Döpel and Kailer [245] have, however, found that triplet lines of mercury may be developed by impact with fast neutral helium atoms from canal rays, the noble gas itself being apparently in an unexcited condition since no helium lines were found in the spectra. This must involve a reaction: $\text{He}^1 + \text{Hg}^1 \rightarrow \text{He}^1 + \text{Hg}^3$ (the superscripts denoting the type of level) in apparent violation of the rule. The anomaly is capable of interpretation when we remember that in this case a strict applicability of the principle is not to be expected since the multiplet splitting is so high. Wigner's contention [237] that the so-called singlet terms are in reality incorrectly defined, and that they represent a case where the spins of the two valency electrons are with much higher probability anti-parallel than parallel and hence correspond rather to triplets, cannot be sustained.

Conclusions as to the applicability of the spin-conservation rule can, for mercury, only be reached by statistical examinations of the various singlet and triplet levels which may be developed, as was done by Beutler and Eisenschimmell [62, 41], but even then the possibility must also exist that the 2^3S_1 mercury atoms have reached this state not by direct excitation as is assumed, but by radiation from higher levels; these may represent either true singlet terms or highly excited states whose characteristics are less clear than those of the lower terms, and further studies should be made upon reactions where these complicatory effects are likely to be absent.

Lees and Skinner [241, 242] have also observed a direct transgression of Wigner's rule in the electronic excitation of some of the helium lines. They find that when a well-defined beam of electrons is passed through the gas at low pressures, the light emitted in the lines $2^1\text{S} \rightarrow n^1\text{P}$ and $2^3\text{P} \rightarrow n^3\text{D}$ is considerably spread outside the electron beam. In the former case, the effect appears to be due to absorption of the corresponding resonance lines ($1^1\text{S} \rightarrow n^1\text{P}$), while in the latter, the only possible mechanism seems to necessitate the collision:



Here then, the rule is clearly violated, and under conditions where owing to the smallness of the spin-orbital coupling the desiderata for the theorem are most fully satisfied. (These papers may be commended for the admirable discussions which they contain upon excitation processes in general.)

It would thus appear that while there is some good evidence for the validity of Wigner's rule, much more experimental work is needed before it can definitely be established or rejected; on the balance of evidence, it would seem that it is in the main justifiable, although like the analogous selection rules, susceptible to variation in some cases. Very probably it will prove to be of much value in the interpretation of observations upon photochemical changes in organic bodies, to which reference is made in Chapter VI.

Interchange of Excitation Levels.

The two D lines of sodium differ in wavelength only by 4 Å, and hence an extremely small energy of excitation. If sodium vapour be illuminated by either alone, this one only appears in fluorescence; but if 0.025 mm. of hydrogen be added, or the temperature be raised to ca. 300° C., then *both* develop. This may to a certain extent be ascribed to pressure-broadening of the incident line (cf. pp. 69-73) but is mainly due to collisional excitation of the neighbouring level. An atom in the upper state may transfer the minute energy difference to another unexcited sodium atom, or a molecule of hydrogen, and then fall to the lower level, the reverse process also being possible [94]. Moreover, if the vapour be exposed to the zinc line at $\lambda = 3303$ Å, the D lines appear very strongly, and the effect is much enhanced by the addition of argon [96, 97]. This must result from photo-excitation of the 3P sodium state, which coincides almost exactly with the zinc line employed, followed by a transition $3P \rightarrow 2D$ in a collision of the second kind either with another metallic atom, or with a molecule of the diluent, as in the former case. Such a process will necessitate the degradation of 1.6 V as kinetic energy, and in accordance with expectation the D lines thus obtained are much less strongly absorbed than in the absence of argon or excess sodium vapour, owing to Doppler broadening.

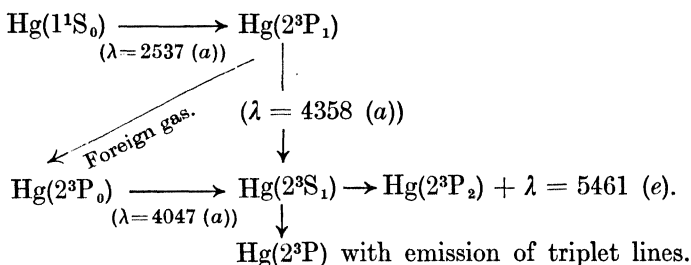
A similar effect has also been found by Wood in mercury [cf. 530, and references there cited], where the line $\lambda = 2537$ can be stimulated by that at $\lambda = 1849$, a transition which, if direct, would violate the selection rule. It cannot well represent an absorption of $\lambda = 10140$ (which may also be present), followed by fluorescence at $\lambda = 4078$, since this last line is not observed, but it might well arise from the processes: $2P \rightarrow 2p_2$ in a collision of the second kind, followed by $2p_2 \rightarrow 1S + \lambda = 2537$, no transgression of the selection principle being involved because of its inapplicability when there is such an intense field between the systems.

A more important illustration of this same phenomenon is ex-

hibited when the same experiment is carried out at 100° C. and over, $\lambda = 2537$ being used as the excitatory radiation. The partial pressure of the vapour is then large enough to enable every excited atom to suffer many collisions during its life period, and deactivation ensues, with a corresponding diminution in the intensity of the resonance radiation.

Again, if the vapour be exposed, at not too low a temperature, and in the presence of a small amount of nitrogen, helium, or carbon monoxide, to the unfiltered light from a mercury arc, strong absorption occurs at $\lambda = 2967$ and 4047 , while $\lambda = 5461$ and a number of lines of the triplet system in the visible and near ultra-violet appear in emission.

Since all of these lines are known in emission in *pure* mercury, although some are in this case very much fainter than when the nitrogen is present, we may conclude that they originate in transitions which are enhanced by the foreign gas, and the mechanism generally accepted for the overall process is :



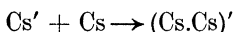
(The affixes (a) and (e) here respectively connote absorption and emission.)

Photoionization in Collisions of the Second Kind.

Since an electron of kinetic energy $Ve = \frac{1}{2}mv^2$ can excite an atom, in an impact of the first kind, to a higher quantum level, from which it returns to its initial state with the emission of a photon of energy such that $h\nu = Ve$, it follows that this quantum, upon absorption by another atom, should be able to perform the same process of excitation. Hence were it feasible to irradiate a gas with a continuous spectrum extending far enough towards the short wavelengths, where $h\nu$ is of the magnitude associated with the ionization potentials found by electron impact, a line absorption should be found, converging to a sharp cut-off at the point where the equivalent $h\nu$ value is sufficiently great to cause the removal of an electron completely from its parent body ; the absorption should then be con-

tinuous. A determination of the ionization potential should thus be possible from purely spectroscopic data, but in practice such is not found to be the case since the continuous absorption tends to extend back into the region of line absorption, most probably due to a Stark effect whereby the fields of the individual atoms mutually interfere and hence induce a shift in their normal series limits [288]. (Other possible causes, such as formation of unstable molecules [290] and the occurrence of forbidden transitions near the limit of the principal series [291] cannot, however, be entirely neglected.) Moreover, the ionization potentials of most gases lie at such high values that the equivalent $h\nu$ quantum corresponds to radiation of a wavelength so short that it lies below the limits of transmission of any substance which can be used as windows for the apparatus; for example, V_i for nitrogen is ca. 16 V, which would necessitate light of $\lambda = 770 \text{ \AA}$, while for helium ($V_i = 24.5 \text{ V}$) the wavelength would have to be as low as 500 \AA . Definite photoionization is in practice restricted, in all probability, only to the alkali metal vapours, where V_i corresponds to wavelengths in the near ultra-violet (approximate values are : Cs $\equiv 3184$, Rb $\equiv 2968$, K $\equiv 2856$ and Na $\equiv 2412 \text{ \AA}$ [99]) and to mercury. It is therefore necessary to detect the onset of ionization when it occurs, by electrical methods, and the evidence of recent years shows that in many cases the mechanism operative includes a collision of the second kind. In the earlier work, the ionization was followed from the appearance of free electrons in the gas under examination, but it is now known that this rarely leads to reliable results by reason of the very intense secondary emission, in a purely photoelectric effect, from thin films of the vapour condensed upon the metallic parts of the apparatus and subjected to the action of stray and scattered light. The best data have been obtained by the use of a molecular beam of the vapour, which after irradiation is rapidly frozen upon a surface cooled by liquid air so that diffusion towards other parts of the apparatus is rendered impossible. The *positive ions* are then caused to diminish the space-charge in the vicinity of an appropriately sited filament, so that when they appear, even in small numbers, a most marked increase occurs in the cathodic emission; this technique has the great advantage of being comparatively insensitive to secondary electron emission, if it takes place at all, while what is virtually a self-amplification of the order of 10^5 is automatically provided so that the electrical measurements are rendered easy. It may be mentioned that this method of space-charge annulment was due in the

first instance to Hertz [100] although others had previously made observations having much bearing upon the subject [101, 102]. [For recent applications, see 289.] Mohler, Foote, and Chenault [103], have found that photoionization of caesium is detectable when the vapour is illuminated by lines of the principal series such as : $\lambda = 3880, 3611, 3480, 3400, 3350$ and 3314 \AA reaching, as would be expected, a maximum at the limit $\lambda = 3184 \text{ \AA}$. The onset at wavelengths greater than the theoretical value (i.e. $\lambda = 3184 \text{ \AA}$) was attributed to collisional ionization of atoms already excited by optical absorption, but Franck and Jordan [104], pointing out that the fraction of impacts which render the reaction energetically possible is far too small to account for the magnitude of the effects which are observed, suggest that the formation of the ion occurs in a two-stage process, viz. : $\text{Cs}' + \text{Cs} \rightarrow (\text{Cs.Cs})'$, followed by : $(\text{Cs.Cs})' \rightarrow (\text{Cs.Cs})^+ + e$; of these steps, the first would be dependent, and the second independent, upon the total pressure, and in a later study Mohler and Boeckner [105] have shown that at any rate the latter condition is satisfied. The ionization is much diminished by the addition of a foreign gas [105], probably due to the degradation of part of the energy of the excited caesium atom upon collision with a molecule of the diluent ; the effective cross-section of the Cs' for this process is apparently close to the ordinary " kinetic " value, whereas that for the other reaction :

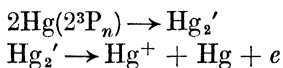


seems to be abnormally large. Similar results have been obtained by Laurence and Edelfsen [342] for rubidium vapour.

The results with mercury are of particular interest because of their bearing upon the phenomenon of excitation and ionization by cumulative action, examples of which are quoted elsewhere (pp. 22, 23). Rouse and Giddings, to whom the work is due [317, 318] guarded against spurious effects from photoelectric emission by using two electrodes of different areas so that if electrons were produced by optical absorption at the surfaces, then the current between the plates would depend upon the polarity ; were the charged bodies formed, however, by ionization as a volume effect, then the current would be independent of its direction round the circuit. On illuminating the vapour with the broad line at $\lambda = 2537 \text{ \AA}$ from a *hot* arc, the ratios of the currents varied as the areas of the electrodes, decreasing with rising vapour pressure ; here, then, the effects seem to be photoelectric in origin. The same was found with a *water-cooled* arc (which gives a narrow line) when the light was led

into low-pressure mercury vapour, but at ca. 0.2 mm. both the ratio and the magnitude of the currents started to change until at 10 mm. the former was nearly unity while the latter were over 100 times as great as those obtained under exactly similar conditions with the hot arc. In this last case, definite photoionization was assumed, especially since positive ions themselves were detected by the Kingdon method of space-charge annulment (*supra*).

The ionization potential of mercury being 10.4 V, a single-step process: $\text{Hg} + h\nu \rightarrow \text{Hg}^+ + e$ is inconceivable, but Rouse and Giddings were able to show that a multi-stage reaction must involve only the 2^3P mercury states since the effects found with the cooled arc could not be reproduced with neighbouring 2P lines such as $\lambda = 2483, 2466$, etc., used either alone or in conjunction with $\lambda = 2537 \text{ \AA}$. As would be expected, the yield of ions varies roughly as the square of the light intensity, although the exponent tends to depend somewhat upon the vapour pressure. The main difficulty in these investigations is to account for ionization from the impact of two 2^3P atoms if Hg^+ only is concerned, since even if we make the unlikely supposition that the highly purified vapour used by Rouse and Giddings could contain enough 2^3P_1 atoms to render the necessary collisions sufficiently probable, the total energy (9.76 V) is still less than that required for ionization, and the fraction of atoms able to contribute the deficiency as kinetic energy is negligible in a gas at only 140°C . It would seem more than likely that here, as in the parallel case of caesium, a molecular ion is formed in a reaction:



but unfortunately nobody has so far made the obvious tests with differential pumping and a Dempster type of mass-spectrograph.* (The probable existence of factors such as this, to say nothing of the metastability of the 2^3P_0 level, and the ability of mercury to form a hydride of relatively good stability, is another reason for regretting that so many studies upon sensitized reactions have been made with mercury.)

Energy Interchange between Excited Atoms and Electrons.

Few attempts appear to have been made to verify the Klein-Rosseland principle for the conditions for which it was first worked

* Since this was written, an extended research has been made by Arnot and Milligan [529], who find that diatomic ions are quite definitely formed.

out, viz. the acceleration of an electron by energy imparted to it upon contact with an excited atom, very probably by reason of the more spectacular successes of the generalized theory in the domains of spectroscopy and other fields of inquiry. Direct verification has, however, recently been obtained. Smyth has sought to decompose the negative ion of iodine by electron impact in the hope that the electron affinity (3.5 V) might be added to the *vis viva* of the bombarding particles, but the results both here, and in similar experiments wherein the activation energy of ozone undergoing thermal decomposition was drawn upon, were inconclusive [332, 333]. Leipunsky and Strauff [4], in some ingenious experiments wherein a supply of ions and excited atoms was provided by phosphorus undergoing oxidation, a beam of electrons being directed through the gas, did find some variations in the electron speeds, but here again the results were not entirely definite. Later work by Latyscheff and Leipunsky [5] was more successful. It was found that a beam of electrons, directed through mercury vapour in the nearly field-free space between the two grids in the usual Franck-Hertz arrangement for the determination of critical potentials, can receive an increment of kinetic energy equivalent to 4.7 V when the vapour is illuminated by $\lambda = 2537 \text{ \AA}$; although the accuracy of the measurements was not, in all probability, very high, this value suggests that the metastable 2^3P_0 mercury atom is here the source of the energy, as would be expected from simple considerations as to the relative concentrations of the upper and lower 2 P states [cf. 161, 121]. Moreover, the maximum probability of the energy interchange was found when 2.7 V electrons were used, so that after acceleration by collision their velocity became equivalent to 7.2 V. This latter observation was considered by Latyscheff and Leipunsky to be direct proof of Klein and Rosseland's subsidiary postulate as to the conditions for the maximum probability of the energy transfer under these particular circumstances [1, 2] since other workers in their laboratories had found that the optimum excitation of the 2 P states by collisions of the *first* kind in mercury also occurred at 7.2 V. Their suggestion cannot, however, be maintained, since concordant investigations for helium [306, 307] and also for mercury itself [308-311] show that the maximum of the excitation function really lies at only ca. 0.1 to 0.25 V above the true energy of the excited state. It would seem likely that we have here to deal with a modified Auger effect (q.v.) wherein a distortion of the potential energy curve of the excited atom is

induced, probably with some interpenetration, by the incident electron, of the outer orbits of the atom, so that, as in the case of ionization by contact, an unstable complex is formed, and then breaks up. This point is, however, of minor importance compared with the general principle which the experiments seem to have established.

CHAPTER III

IONIZATION BY ELECTRON TRANSFER

It was discovered by Harnwell [136] in 1927, that the proportion of one ionic species to another in mixtures of the noble gases of constant composition and submitted to a discharge is markedly dependent upon the overall pressure; a similar effect was found, about the same time, by Hogness and Lunn [138] in mixtures of argon and nitric oxide. For example, under given conditions of excitation, the ratio He^+/Ne^+ in a 1 : 1 mixture of the gases fell

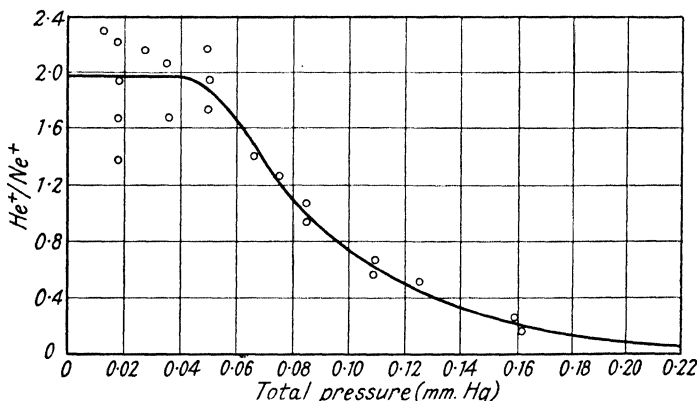


FIG. 6.—Ratio of He^+/Ne^+ as a function of pressure (Harnwell).

from 1.7 at 0.06 mm. to ca. 0.1 at 0.20 mm., while below 0.04 mm. the results were somewhat irregular but indicated a much smaller influence of pressure upon the relative proportions of the two species (Fig. 6). It was concluded that the formation of the ionized neon here involves a collision process, and since the *vis viva* of the helium ions was too small to produce Ne^+ as a purely kinetic effect (*vide infra*), the reaction must necessitate an electron transfer in a collision of the second kind. (The concept is by no means a new one, J. J. Thomson having by its means explained apparent variations in the $\frac{e}{m}$ value at different points along a

beam of positive rays ; Franck has also used it to account for the change of charge of canal rays, taking into account the electron affinities of the atoms concerned [340].)

The phenomenon has been very extensively studied, in spite of the numerous experimental difficulties, notably that of securing a constant source of positive ions for the primary beam when metallic ions are to be used, and found of quite general occurrence.

The apparatus needed falls into two parts, viz. a source of positive ions and secondly, an analysis chamber. For the former, discharges are used, as in ordinary positive ray work, if gaseous ions are desired ; if metallic ions, the Kunsman sources are employed, or much better, the thermionic devices mentioned on p. 59, wherein the rate of generation of the ions is controlled by the filament temperature. The ions then pass from the "gun" through the usual slit system into the detection chamber where both the primary beam and its reaction products are analysed by one of the methods upon which Dempster and Smythe and their associates have done so much valuable work [37, 99] i.e. determination of the number of ions arriving at a target enclosed in a Faraday cylinder and connected to earth through a high resistance across which an electrometer is shunted. The nature of the ions being recorded is known, as usual, from the strengths of the deflectional magnetic and electric fields, while the area enclosed by the peaked curves obtained when one of the fields is plotted against the current to earth, gives their number ; an increase or decrease in their concentration leads to a proportional enlargement or shrinkage of the area, as the case may be.

Kallmann and Rosen [137, 293, 351] and Duffendack and his associates [243, 264, 265] have in this way found many examples of electron transfer, and extend Harnwell's conclusion as to the greatest probability of the interchange when the ionization potentials of the reacting bodies are closest to each other, to the suggestion that the effect is at its maximum when the primary ions are projected into the company of their own molecular species. For example, in an often-quoted experiment where N^+ and N_2^+ were the initiators of the reaction, Kallmann and Rosen found that with nitrogen as the "reagent" gas the concentration of $N_2^+(V_1 = 16 \text{ V})$ fell off much more, as the pressure was decreased, than did that of $N^+(V_1 = 14.5 \text{ V})$, and a similar effect was obtained when the ions were led into argon ($V_1 = 15.7 \text{ V}$). Neon ($V_1 = 21.5 \text{ V}$) and helium ($V_1 = 24.5 \text{ V}$) had little effect on either

N^+ or N_2^+ with oxygen ($V_1 = 13$ V), however, the atomic ion was much more diminished in numbers than its molecular relative, but even then the reduction was not comparable with the extent of removal of the N_2^+ by neutral molecular nitrogen in the first case just mentioned. A somewhat similar effect has been observed by Brasefield [139, 246], who took especial precautions against the secondary electrons, which are so often a source of trouble when studies are being made upon ionization phenomena.

Ionization of the Noble Gases by Ions of the Alkali Metals.

The interaction of alkali metal ions and the noble gases has led to results which are so far but very imperfectly explained. It

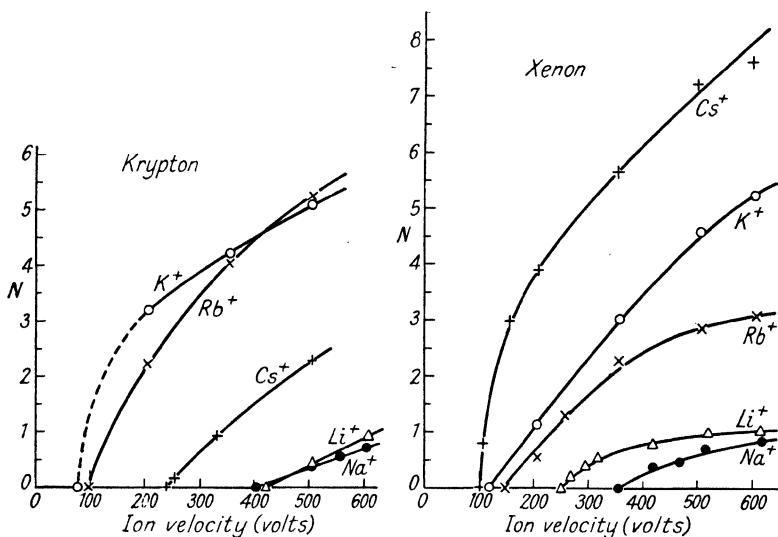


FIG. 7.—Onset of Ionization by Electron Interchange in Kr and Xe (Beeck and Mouzon).

was discovered by Beeck in 1930 [140], and has since been amply confirmed [e.g. 140*b*], that in general the maximum ionization is produced, and commences at the lowest voltage, when the impacting ion has as its partner that noble gas which is its nearest neighbour in the Periodic Table and hence has most nearly the same mass and the same number of electrons (Fig. 7). Krypton is apparently anomalous in this respect, since below 400 V it is more strongly ionized by K^+ than by Rb^+ [141, 143, 247, 248, 292]. Moreover, the *absolute* efficiency of ionization, as measured by the number of electrons liberated per primary ion/cm.path/mm. pres-

sure, increases with the atomic number of the gas concerned, i.e. it is 3.4 for K^+ in Ar, but 7.2 for Cs^+ in Xe [140, 141, 143]. The effects are illustrated in Table 5, taken from a paper by Beeck and Mouzon [248], while Fig. 7 shows the sharpness of onset of the induced ionization [141].

TABLE 5

| | | Li+ | Na+ | K+ | Rb+ | Cs+ | |
|--------------|----|-----|-----|-----|-----|-----|------------------------------------|
| Noble gas | Ne | 307 | 175 | 320 | 420 | 437 | Ionization Potential (Volts) |
| | Ar | 100 | 105 | 95 | 180 | 365 | |
| | Kr | 420 | 400 | 80 | 100 | 143 | |
| | Xe | 250 | 360 | 120 | 145 | 105 | |

Frische [142] has studied the effects of K^+ on Ar, Ne, He, N_2 , CO, H_2 , and Hg, using accelerating voltages (V_a) of up to 4,000 V. At this point, the curve for number of secondary ions produced vs. accelerating potential, quite definitely shows saturation for Ar, and not quite so certainly the same for Ne; with CO and N_2 the effects are much the same as with Ne, as would be expected from their structures, but with H_2 and He the induced ionization is scarcely detectable and appears only with high V_a values, such as 1,600 for H_2 . As regards these last, the observations are well in accord with earlier results, which showed that ionization of the light gases by similar ions, only sets in when the projectile bodies are very fast [300]. Moreover, when the "effective energy" of the ion is evaluated by taking into account the kinetic energy of the ion-atom system relative to its mass centre, all the ionization potentials thus obtained lie within a small range and generally at less than 100 V [142].

It will, of course, be realized that an ion should be able to cause ionization upon impact purely as a "kinetic" effect, the same applying to a neutral atom. If the masses of the impacting and target bodies be M_1 and M_2 , their velocities before the collision u_1 and u_2 , and after the collision v_1 and v_2 , then for the conservation of energy we have:

$$\frac{1}{2}M_1u_1^2 + \frac{1}{2}M_2u_2^2 = \frac{1}{2}M_1v_1^2 + \frac{1}{2}M_2v_2^2 + W,$$

where W is the work done, in ergs, in the ionization process, and for the conservation of momentum: $M_1u_1 + M_2u_2 = M_1v_1 + M_2v_2$. This gives $W = \frac{1}{2}(u_1 - u_2)^2/(1/M_1 + 1/M_2)$, or if the denominator be written $1/\mu$, then $W = \frac{1}{2}\mu(u_1 - u_2)^2$. Now if the target body

be at room temperature, its energy and momentum will be very small compared with that of another accelerated through a field of some tens of volts or more (the kinetic energy of a molecule at 20° C. is only 38 millivolts), and so the expressions reduce to $\frac{1}{2}u_1\mu^2 = W$, or, if the bodies be of the same mass, then $\frac{1}{2}Mu_1^2 = 2W$; that is, an atom (or ion) which is to ionize an atom of its own species in a collision of the *first* kind must at the moment of impact be moving with a velocity equivalent to twice the ionization potential. This is exemplified by Brasefield's observations [139] that ionization of argon by impact of neutral atoms commences at ca. 40 V, while for neon and helium under the same conditions it may first be detected at 50 and 60 V respectively, all of these critical values being about twice the normal ionization potentials [cf. p. 11]. In general, if m be the mass of the projectile particle and M that of the target whose ionization potential is V_1 , then the minimum accelerating potential V_a at which "kinetic" ionization will set in is given by :

$$V_a = V_i(1 + m/M). \quad [\text{See also 144, 297-299.}]$$

If, on the other hand, the ionization follows merely as a result of the redistribution of potential energy of the system in a reaction : $A_p^+ + A \rightarrow A_s^+ + A$, of the type envisaged by Harnwell, then no change in the kinetic energies of the bodies would seem necessary, so that when it occurs a beam of slow "primary" ions A_p^+ is converted into one of neutral atoms—which cannot be detected by positive ray methods—while the "secondary" ions A_s^+ are left to drift with the small velocities associated with room temperatures. The effect should thus be detectable with very low ion velocities, and Wolf [302] working with the type of apparatus used by Sutton [227-229] for the determination of ionization-functions of alkali metals, finds that an "Umladung" in argon sets in at ca. 20 V, rising steeply to a maximum at ca. 40 V, and thence falling away; ionization by *impact*, as distinct from *contact*, sets in at some 300 V, and then rises slowly, although the effective cross-section of the neutral atom for this process is at its best only about one-seventh of that for the electron interchange. Dempster has also observed that protons accelerated over the range 14 to 930 V can pass through helium practically without any loss of energy, although each one would on the average undergo 120 collisions, whereas He^+ under the same conditions is strongly absorbed, neutralization occurring at almost every impact [334, 335].

Investigations show, however, that "impact" ionization rarely

occurs, since no ionization of argon by potassium is detectable at less than 95 V [140], although the masses of the two atoms are practically identical, indicating that nuclear charge must have a great influence upon such processes [see also 277]. To emphasize this point, the appearance potentials of the various noble gas ions calculated for *impact* of alkali metal ions are given in Table 6, which may be contrasted with Table 5, wherein the results of Beeck and his associates are shown.

TABLE 6

| Noble Gas. | Li+ | Na+ | K+ | Rb+ | Cs+ | |
|------------|-----|-----|-----|-----|-----|-----------------------------|
| He | 67 | 165 | 263 | 545 | 840 | " Ionization potential " |
| Ne | 29 | 46 | 63 | 113 | 164 | |
| Ar | 18 | 25 | 31 | 49 | 68 | |
| Kr | 15 | 18 | 20 | 28 | 36 | |
| Xe | 13 | 14 | 15 | 20 | 24 | |

The discrepancies most probably arise out of the neglect of other factors such as the polarization of the ion, and the probability of recapture of the electron set free by one or other of the positive ions, the three-body nature of the reaction tending to favour the recombination, at any rate to a certain extent [297-299].

There are, moreover, uncertainties attaching to the experimental technique of these researches which suggest, according to some authorities [336] that the absolute values for the rate of disappearance of the " primary " ions—and the critical potentials for the onset of induced ionization—should be regarded with a certain scepticism. We encounter here what is clearly one of the circumstances wherein the effective cross-section is indeterminate and evidence is available to show that the absorption of ion beams may be dependent upon the geometry of the apparatus [see 337, 338]. The absorption of Li^+ by mercury is in fact very much controlled by the experimental arrangements [339], and there can be no doubt that small-angle scattering represents an important factor which so far does not seem to have been taken much into account, although Beeck [296] recognizes its possible influence. Moreover, diatomic gases may be dissociated, as in Kallmann and Rosen's experiments with hydrogen [cf. 37], while another possibility is that the bombarding ion may merely suffer a change in its velocity without undergoing " Umladung," although with some types of apparatus

the latter process would appear to be that taking place. This has been observed by Kennard [277] in studies upon the neutralization of Cs^+ and Na^+ in hydrogen, helium and argon. A beam of 35 V caesium ions in hydrogen or helium is slowly weakened by neutralization or scattering, whereas 90 V ions are merely retarded with an energy loss of ca. 1.3 V at each collision. In argon, the ions are rapidly neutralized with mean free paths only 2 or 3 times that of a xenon atom in the same gas. Sodium ions are but little affected even at 455 V.

Theories of Electron Interchange.

The theory of electron interchange when the systems are fairly closely in resonance was first outlined by Kallmann and London [8], and although they neglect any contribution of kinetic energy possessed by the bodies [see 9] their results are in general in harmony with the experimental observations. They suppose that when two bodies A and B approach to each other, one being ionized, then the most loosely bound electron in the neutral atom will oscillate between A and B, the probability Q that it will be at A at time t if at $t = 0$ it was at B, being given by :

$$Q = \frac{\beta^2}{1 + \beta^2} \cdot \sin^2 \frac{\pi}{h}(S + W_{AB} - W_{BB}) \sqrt{1 + \beta^2} t,$$

where $\beta = 2W_{AB}/(S + W_{AA} - W_{BB})$. The quantities W_{AB} , W_{AA} and W_{BB} are interchange integrals (W_{AB} being that specifically associated with the electron transfer from A to B) and are functions of R , the distance separating A and B at time t , while S is the difference between the neutralizing energy of the ion (i.e. its ionization potential with the sign changed, assuming an unexcited ion) and the ionization potential of the neutral atom. The period of oscillation of the electron is then equal to :

$$(S + W_{AA} + W_{AB})/2h.$$

The effective cross-section for electron interchange, which is a measure of the likelihood of the reaction, can be worked out from these expressions and depends upon S and the mean interchange integrals and hence upon R as well. When $S = 0$, this likelihood, Q , is at a maximum, and varies inversely as the $2/3$ power of S in either direction ; W_{AB} diminishes as the inverse exponential of R and hence Q becomes rapidly smaller with S . The curve in Fig. 7 is obtained in this way, and although it may in general be justifiable only as regards general form, since it presupposes that the W 's have all the same values as for H and H^+ , the system for which

Kallmann and London first worked out these ideas, it does show that Q is greatest when S is small and that the optimum effects may be expected when a gas is being exposed to its own ionic species, in accordance with the experimental results.

The likelihood of interchange of the electron is not, however, so dependent upon the magnitude of S when the primary ion is an atom A^+ and the other body a molecule B , since an excess of energy can be taken up in the vibrational states of the latter ; moreover,

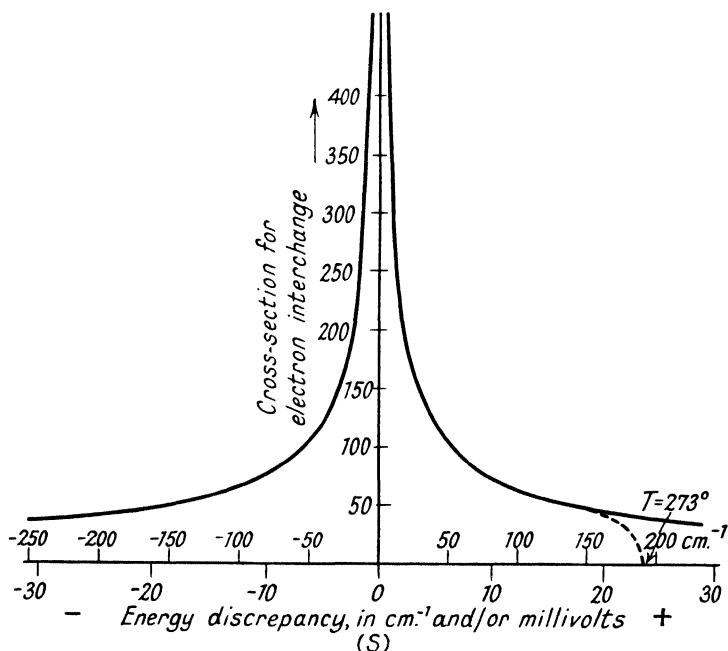


FIG. 8.—Cross-Section for Energy Interchange as a Function of S (Kallmann and London).

instead of the chance of the transfer taking place being a symmetrical function of the positive or negative value of S , as Fig. 8 shows, the process $A^+ \rightarrow B \rightarrow B^+ + A$ tends to predominate, i.e. the reaction develops, as it were, a bias towards non-reversibility. In this case, an electron transfer may be accompanied by changes in the *vis viva* of the bodies concerned, as in other collisions of the second kind and such processes are, if anything, of more general occurrence than the simple one : $A_p^+ + A \rightarrow A_s^+ + A$, (where A_p and A_s are respectively the primary and secondary atom ions) which, if scatter-

ing can be neglected, does not involve any change in translational velocities among the participants.

The idea of a shared-electron complex, which is what Kallmann and Rosen's theory involves, has also been utilized by Zwicky [148] to explain the phenomenon of electron transfer. He suggests that the conclusions can best be explained on the assumption that when an ion m approaches close to an atom M , then by reason of the low translational velocity of the former as compared with an electron of the same kinetic energy, the two bodies will be in the range of each other's field for a period which exceeds that of the rotation of one of the electrons so that they inter-penetrate and give rise to a complex quasi-molecule. The atom then suffers an adiabatic disturbance in the form of an elastic wave, which may so affect the most loosely bound electron that this is ejected and recaptured by the ion, presumably in a kind of Auger process (*vide infra*). The potential at which the ionization sets in will therefore be determined by the characteristics of the complex, whence, for example, it is possible to explain the decrease in the voltage at which ionization sets in *pari passu* with an increase in the masses of m and M ; the work required to detach an electron from the quasi-molecule will tend to change in the same manner as the ordinary ionization potentials of the reacting bodies, which fall with increasing mass in any one family in the Periodic Table. In a similar way, it follows that the ionizing power of an impacting atom will fall with decreasing mass if its kinetic energy and the mass of the other atom are maintained constant. The theory has been criticized by Frische [142] who finds that the gases which ionize most readily are those which are most efficient as scattering agents, whereas Zwicky's suggestions necessitate head-on collisions since the probability of ionization decreases with the extent of momentum transfer, but it seems worthy of mention as an attempt to describe the phenomenon in terms of simple concepts and without resort to methods such as those of quantum mechanics which are frequently, as Barnes has said [231]—albeit in another connection—a scandal to human thought.

A more refined approach to the problem has been outlined by Weizel and Beeck [149], who suggest that for the case of helium being ionized by Li^+ a complex may be formed which will be analogous with one of the excited states of diatomic helium and permit of subsequent dissociation to He^+ and neutral lithium. We may first consider the physical principle upon which Weizel and Beeck base their theory.

Consider an atom which is ionized in one of its inner shells ; for definiteness let us say the K-shell. Under such conditions, an electron may jump from one of the higher levels (e.g. the L-shell) into the vacant space in the K-shell, the emission of energy consequent upon the transition taking place either through radiation or by ejection of another electron ; the latter process constitutes the phenomenon first convincingly established by Auger and now known by his name [303, 371–374].

The effect as it occurs in the inner shells of an atom thus involves *two* electronic transitions, one of which leads to the emission of a definite X-ray line ($K\alpha_1$ in Fig. 9) but the other to electrons having an “energy-spectrum” since they may originate in any one of a number of levels L_I , L_{II} , M . . . etc. Formally considered, the

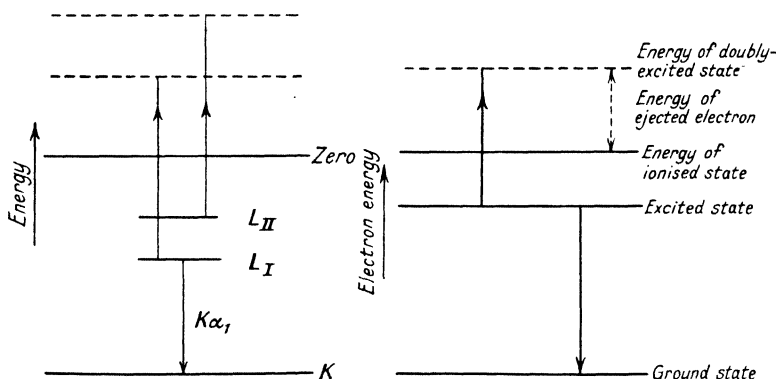


FIG. 9.—The Auger Effect.

Auger effect corresponds to the emission of an X-ray quantum, and its subsequent re-absorption by the parent atom, i.e. to a process of internal conversion of atomic energy. So far, there is no experimental method to show whether the effect is due, as suggested, to the liberation and recapture of an energy quantum, or to direct interaction of two inner electrons ; theory indicates, moreover, that there is no hard and fast division between the two processes [375–377]. In intensity, the Auger effect is small compared with the strength of X-ray emission when the primary ionization is effected by hard X-rays, but large where soft rays are concerned ; in the ultra-soft region it is sometimes very hard to obtain secondary X-radiation at all. One could in principle envisage an Auger effect in the region of optical excitation if *two* electrons were excited, e.g.

in mercury ; although direct experimental evidence upon the point is so far lacking, the concept, expressed in terms of potential energy curves, will readily be understood from what follows. In general, Weizel and Beeck consider the potential energy curves for the normal and ionized states to intersect (Fig. 10a) to provide a region wherein a radiationless transition from the initial state to the ionized condition may take place, with the separation of the extra electron ; this, for small internuclear distance, is very probable. It is, however, also conceivable that the normal curve might cut another (Fig. 10b) so that after the separation a doubly excited helium atom

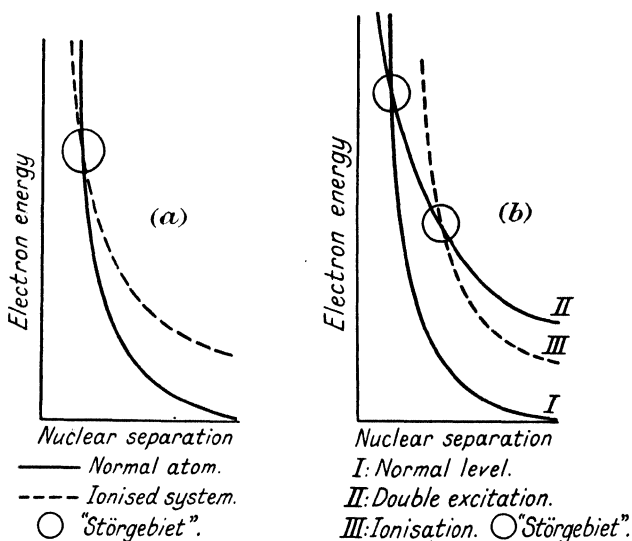


FIG. 10.—Ionization by Contact as an Auger Effect (Weizel and Beeck).

remains, the Auger effect entering either during or after the separation of the systems, a singly ionized atom resulting from the process. (It would seem that this should occur not merely in the Störgebiet but anywhere to the right of it.) Now in order to provide for the close approximation of the two bodies, kinetic energy must be present in one of them of magnitude great enough to overcome the electrostatic repulsive forces, and this clearly in excess of the ionization energy of the noble gas concerned. The concept has been developed by Stueckelberg [287] who, making reasonable assumptions as to the positions of the intersections of the potential energy curves, obtains results for the ionization of argon by K^+ which are

in good agreement with the experimental results of Nordmayer [292].

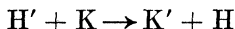
The wave-mechanical view has been stated by various investigators, of whom Massey and Smith [232] appear to have made the greatest progress. The relative velocity of the two atoms being small compared with that of their electrons, the former are treated as if initially at rest so that the interaction effects can be introduced to their wave functions. The relative motion then being applied as a perturbation, they derive equations which to some extent take into account the interaction of the various stationary states of each system and, assuming that the exchange energy and polarization are of small moment compared with the Coulomb forces, obtain expressions which fit the data for the scattering of protons in helium and argon to quite a reasonable degree of accuracy, although for small angles, classical theory, taking into account the forces other than Coulomb, gives better results. With further assumptions as to the distortion of the wave equations by the interactions as a function of the distance separating the two particles, and also as to the final electronic wave function being that of the undisturbed systems, additional expressions are obtained for the cross-sections for excitation and capture by protons in helium which also fit the observations much better than others using such devices as Born's approximation. This theory now indicates that the probability of an inelastic collision is negligibly small unless the kinetic energy of relative motion exceeds a certain critical value, which may be very much larger than that required for the process to be possible on energy considerations alone, and somewhat analogous with the familiar physicochemical concept of energy of activation. (The parallelism is not, however, quite exact, since the "chemical" activation represents the energy required for the production of a state of low excitation—say 2 to 3 V—whereas Massey and Smith's is more strictly a relative velocity large enough to overcome the tendency for the collision to be more or less adiabatic.) The existence of this activation potential thus necessitates a sharp onset of ionization and excitation when ions themselves are employed as the agents, and this has very definitely been observed both in noble gases bombarded by alkali metal ions [140–143] and also for excitation of the helium 4^1P state by hydrogen canal rays and electrons [233].

In these last experiments, due to Döpel, low accelerating potentials favoured excitation of the hydrogen, whereas at higher voltages

the effects were reversed, in accordance with prediction. Similar studies upon the excitation of Na, K and Hg by the mixed canal ray beam showed that whereas the heavy atoms were strongly affected, the hydrogen atoms themselves were practically uninfluenced. This is explicable by the expression for the activation energy :

$$E_c = M(\Delta E)^2 r_0^2$$

where E_c is the activation energy, M the reduced mass of the system, r_0 the nuclear separation, and ΔE the excitation potential concerned. The ratio of the activation potentials thus being equal to the square of the ratios of the excitation potentials, the probability of K being excited by H is some seventy times as great as that of the reverse process, and even for Hg the factor is ca. 4. The increase in the *absolute* magnitude of the activation potential for the reaction :



as compared with the parallel case : $H + He \rightarrow He' + H$ follows from the fact that r_0 is much larger for the heavy atoms. Neutral atoms, it may be noted, are apparently better ionizing agents than the corresponding heavy ions, owing to a decrease in r_0 through the screening effects of the outer electrons. The theory also offers some interesting deductions as to the exact nature of the processes involved in the absorption of proton beams by other gases, upon which measurements have been made by Ramsauer and his co-workers [235]. The reaction cross-sections measured for low proton velocities must be those for small-angle scattering, which the experimental arrangements could not here detect. They will decrease rapidly with rise in the proton velocity, when even elastic collisions result in deviations large enough to be determined, and excitation and capture processes are still too small to become manifest. Still later, however, these last set in with increasing probability, and when the rate of increase of the inelastic cross-section equals the rate of decrease of the elastic cross-section, the minimum appears in the experimental curves (Fig. 11). Furthermore, the magnitudes of ΔE for the process : $H^+ + G \rightarrow G' + H^+$, where G is a gas atom show that the activation energy for $H^+ + He \rightarrow H' + H^+$ should be higher than that for $H^+ + Ne \rightarrow Ne' + H^+$, which in its turn will be greater than that for the remaining noble gases, so that the minimum should occur at a higher voltage for He than Ne, and higher for Ne than for Kr and Xe, a conclusion also supported by observation. (The large activation energies for He and

Ne naturally explain their very small cross-sections for collisions with protons. Further observations by Ramsauer upon the products of injection of a proton beam into sundry gases have shown neither slow ions nor electrons at low proton energies, although as the proton speeds were increased, slow ions appeared, due to electron transfer; even at the highest energies used, however, no slow electrons could be found, indicating that kinetic ionization by the protons was negligible, all of the results being again those to be expected from the theory under consideration. [See also 236.]

An experimental test of the theory has been made by Smith [234] by measurement of the capture cross-sections, for various energies, of He^+ in helium, and H^+ in hydrogen and helium. The method

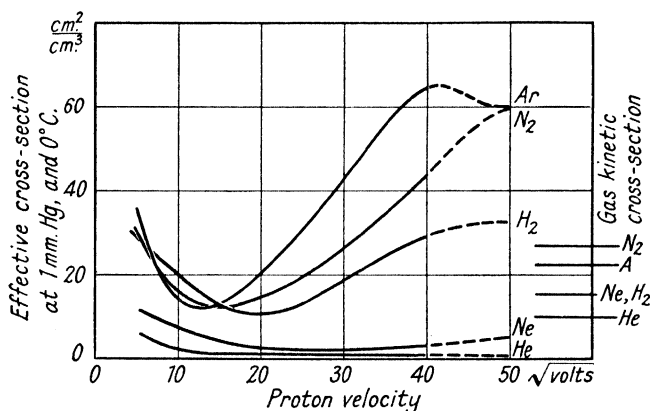


FIG. 11.—Effective Cross-Sections of gases towards protons of various velocities (Ramsauer *et alia*).

adopted was to observe the exponential decrease in a beam of ions passing through the gas, using collectors with wide slits so that very little of the observed absorption was due to elastic scattering. No velocity analysis of the beam was made after it entered the gas concerned, so that practically all of the loss from the beam was due to true capture. The results as observed and calculated from the equation of Massey and Smith are given in Fig. 12, and show that the agreement is fairly good, the discrepancies at the higher velocities probably being due to uncertainties in the interaction energies as used in the case of close approach. For protons in helium and hydrogen the general shape of the curves followed expectations, but owing to the inevitable leak of hydrogen from the discharge tube into the helium through the slits, actual measurement of activation

energy for the electron interchange reaction was not possible. There seems little doubt that electron interchange, when more fully understood, will prove of much importance in explaining many discharge phenomena which at the moment seem somewhat anomalous. As an example, the work of Mitchell and Ridler [304], upon ionic mobilities in nitrogen, may be quoted. Using the standard methods developed in the admirable researches of Tyndall and his school at Bristol, they have found that the addition of as little as 0.018 per cent of mercury to pure nitrogen will induce a large suppression of N_2^+ or an equally pronounced removal of Xe^+ when even 1 per cent of this gas is also present ; similar effects were noticed with krypton

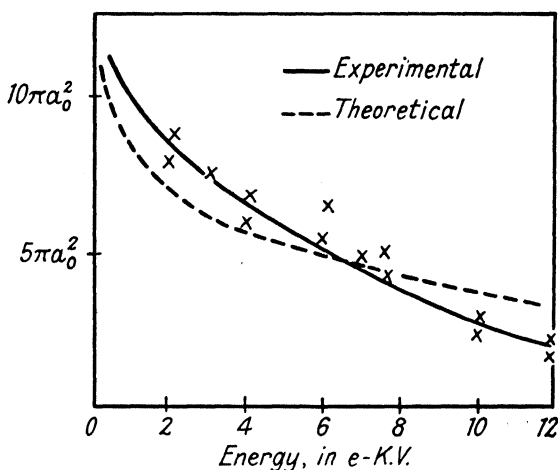


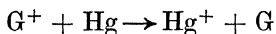
FIG. 12.—Capture Cross-Sections for He^+ in He (Smith).

under the same conditions. It would seem likely that this apparent absorption may partly be due to an actual inhibition of Xe^+ and N_2^+ in the discharge, since mercury, with its low ionization potential (10.4 V) may act as a virtual "brake" upon the electron speeds so that these latter never attain the velocity requisite to the ionization of the noble gas or the nitrogen, but the lower value of V_i might also render quite possible an interchange reaction of the type studied in the preceding pages. Support for this view is given by the fact that the mobilities of no less than 17 ions in nitrogen are all connected in quite a simple manner with their masses, the only exception being N_2^+ itself ; the 7.5 per cent discrepancy between the mobility expected, and as actually observed, seems to be due to electron interchange. The same kind of effect may also be respon-

sible for the genesis of many peculiar atomic and molecular species such as free radicals. For example, the methyl radical (CH_3), which seems to be present in discharges through methane, may be expected to arise through the reaction :



the ionization potentials of methane and methyl being 14.5 and 15.5 V respectively. Such a process, or one of direct excitation in a collision of the second kind, may well be the cause of the large reductions in breakdown voltage which can be induced, in some cases, by addition of a small amount of one of the noble gases. The rather high running voltages generally required for cold-cathode discharges in mercury can be much diminished if a few mm. of argon or neon be added, due to generation of Hg^+ through the reactions :



where G is the noble gas concerned. The principle is frequently utilized in the construction of commercial mercury lamps and arc rectifiers, but care is essential owing to possible complications due to secondary electron emission from the metal surfaces under the impact of metastable atoms. Traces of hydrogen are very inimical, owing to preferential ionization or dissociation of this impurity [cf. 284].

CHAPTER IV

COLLISIONS OF THE SECOND KIND AT GAS-SOLID INTERFACES

Emission of Electrons under Impact of Metastable Atoms.

In the course of his experiments upon the determination of τ for the excited states in mercury Webb [152] found that the time interval between excitation of the mercury and the arrival of the radiation at the photoelectric surface is of the order of the time required for an atom to diffuse from the zone of excitation to the photoelectric system, i.e. ca. $2 \cdot 10^{-4}$ sec., which is very suggestive that the mercury atoms traverse the apparatus in a metastable condition to eject electrons on impact with the metal surface of the photoelectric target. Miss Messenger [153] has also shown that a number of the excitation levels found by Franck and Einsporn [244] using their tetrode circuit in conjunction with mercury vapour, are in reality due to secondary emission of electrons derived from collisional deactivation of metastable atoms at the metallic parts, which confused the points of inflexion in the current potential curves and led to the assumption of a number of states for which there is no spectroscopic evidence. Couliette [154] finds that these metastable atoms can travel considerable distances in mercury under very varied experimental conditions [cf. also 278]. The phenomenon has been fully investigated by Oliphant [155] in some very elegant experiments designed at first to study the effects of positive ions of helium colliding with molybdenum. It was found, however, that the emission from the target, clearly electronic, persisted when all of the ions were filtered out from the impinging gas beam, and that it was due to neutral atoms formed by recombination of ions and electrons and in the high energy state characteristic of such bodies immediately after formation [cf. 274]. In the case of helium, the metastable 2^3S level lies only some 4.7 V below the neutralizing energy of the ion (24.4 V) and if an electron were ejected from the metal, following deactivation of this atom in a collision of the second kind, the maximum energy, V_{\max} , with which it could emerge would equal $19.7 - \phi$ volts, ϕ being the work function of the metal used

as the target. By applying a retarding potential to the electrons thus produced, Oliphant showed that this condition is satisfied. From the approximate constancy of the emission with various metals under given conditions of excitation, i.e. with a fixed concentration of metastable atoms, it was concluded that very probably every impact can be made to result in deactivation, but the extent to which this occurs varies with the depth of penetration, the number reflected increasing as the speed and glancing angle diminish. The kinetic energy of the atoms does not seem to influence the velocity with which the electrons are emitted. Studies by Sonkin [349] upon electron emission due to the action of metastable mercury atoms (2^3P_0) show that with tungsten the results are markedly dependent upon the vacuum conditions and the extent to which the metal has been cleaned and degassed. An absorbed layer of mercury is always a prerequisite for the action, and the final steady state does not apparently set in until a complex, but stable, mercury-oxygen layer has been built up. The efficiency of impact upon this "normal" surface is only ca. 1-2 per cent, and the process does not seem to be influenced by irradiation of the surface to the point of photoelectric emission.

This liberation of secondary electrons is very troublesome in some cases, and there is no doubt that many measurements upon discharges have been vitiated by it, particularly where gases which have metastable states are being considered; Found [156, 350] has shown that it may be as high as one-third of the positive ion current in the positive column of a discharge in neon. It may be noted that secondary electrons can also be emitted from *insulators* under the impact of very fast electrons. The spots of green or blue light which sometimes appear on the walls of hard X-ray tubes are ascribed [159] to cathode rays which have wandered due to the very intense fields and, by inducing some secondary emission, led to the formation of foci, positively charged *vis-à-vis* the cathode. The local heating which ensues frequently leads to the formation of cracks and the breakdown of the tube. The author is indebted to Dr. M. L. E. Oliphant for the information that recent experiments of his show that both glass and quartz become charged up to a potential of ca. 14 V when exposed to a beam of metastable helium atoms, so that it seems that insulators can show a work-function, like metals.

Emission of Electrons under Impact of Positive Ions.

When ions of the alkali metals are directed upon targets of other substances such as nickel, aluminium, etc., a faint emission of elec-

trons may be observed, commencing at a fairly sharp accelerating potential and much enhanced by the presence of a film of gas on the surface, although it never corresponds to more than a fraction of the number of bombarding particles [160–162]. The effect is also scarcely detectable in mercury vapour when a nickel collector is employed [163]. Penning has, however, found [164, 165] that controlled ions of neon or argon can liberate electrons from a number of metals at extremely low velocities (e.g. 7 V for Ne^+ in some cases) and the perfectly linear relation between the likelihood of such emission and the speed of the ions down to the lowest accelerating potential employed seems to indicate that the effect will occur at zero velocity. It is considered likely that emission will occur whenever the inequality $V_i > 2\phi$ is satisfied, since the ion must be able to extract one electron for neutralization and another for ejection. Although the results may be to a certain extent too high by reason of the action of metastable atoms, as suggested by Oliphant [155], it is very significant, as Compton and Langmuir point out [166], that cold cathode discharges in mercury require a surprisingly high voltage in comparison with other gases of higher ionization potential, which on Penning's theory would be due to the comparatively small ability of the mercury ions to induce electron emission since the difference in V_i and 2ϕ is only some 2 V. It is suggested that the effect should be more pronounced in similar discharges in potassium vapour, provided that the cathode is not contaminated with gases or with materials which can adsorb potassium and thus lower the true work-function. A very comprehensive study of the subject has been made by Oliphant and Moon [167] and their conclusions will be examined in some detail. The theoretical treatment is essentially classical in character, but needs little, if any, modification to be brought into line with more recent concepts based upon quantum mechanics. For this later development, readers are referred to the Bibliography [527, 528].

It is clear that a potential barrier must exist near the surface of a metal, since were it absent the free electrons would merely diffuse away into space. This barrier can be regarded as twofold in structure, one part, of magnitude μ , being attributed to space-charge on the formal assumption that electrons *do* pass out of the interior and rapidly establish a condition in which the mutual repulsions of the electrons which have left and are leaving is large enough to hold down the actual emission to an infinitesimally small degree; the other part, which lies farther away from the interface, is due to

image attraction, while an intermediate zone probably has characteristics which may be ascribed to both causes although it is not as yet amenable to calculation. This can account for the ability of positive ions to remain adsorbed on, or in very close contact with, a metallic surface, since the space-charge represents a repulsion while the image force is equivalent to an attraction for both ions and electrons. Moreover, the space-charge field is limited to a zone very close to the surface (probably 10^{-8} cm.) whereas the overall barrier may be detected ten times this distance away and corresponds to $(\mu + \phi)$, ϕ being the work-function and in magnitude equal to ca. $1/5 \mu$. (ϕ cannot, as Oliphant and Moon point out, be identified with the image-force portion of the total barrier, and considered from the standpoint of the Sommerfeld theory, is an incidental fact of experiment, owing to the particular mechanism to which the barrier is due. There is, however, a definite relation between μ and E , the average energy of the electrons in the metal, but its precise form is not germane to the present study of the subject. It may be mentioned that the values of $(\mu + \phi)$ are not very well established in the majority of cases, but for nickel it is ca. 18 V, giving ϕ as 3 V on the supposition just quoted, as compared with the 4.3 V of experiment.) These considerations have been applied in conjunction with theories of Fowler and Nordheim [168, 169] upon the electrical conditions at a metallic surface, to obtain the probability that a positive ion will be able to extract an electron by virtue of its field and lead to autoelectronic emission, the process being formally regarded as one of transition of an electron through the potential barrier to a state of equal energy associated with the ion. The variation of energy of an electron between a metal surface and an ion in close proximity thereto, is represented in Fig. 13, the left- and right-hand curves respectively having reference to the electron in association with the metal, and with the ion, and the metal surface being idealized to a true plane. It follows from this, that, unless the ion approaches very closely to the surface, an electron cannot penetrate the barrier and combine with the former unless through the agency of the "tunnel" effect of the wave mechanical theory, but the existence of the phenomenon will render possible the desired transition provided that X corresponds to an energy level of the resulting atom, the perturbation of the ion-field by the metal broadening the "width" of the levels concerned and thus facilitating the process. This can account for the ease with which ionized helium is converted into metastable atoms on contact with outgassed

platinum, since the difference between the energies of the body formed by ion neutralization and that of the nearest stable atomic level is only some 0.06 V, which may be less than the "width" of the perturbed 2^3S state (*vide supra*).

The probability that an electron will penetrate the potential barrier depends only upon its positive kinetic energy, but the level to which it will go in the atom is determined by the total sum of this and the negative potential energy; since the high energy states characteristic of the ion are those which extend farthest from it, the effective width of the barrier is least for these electrons which have the highest values of μ , which are also the most numerous, and hence may be regarded as the ion-neutralizing agents. When the ion is

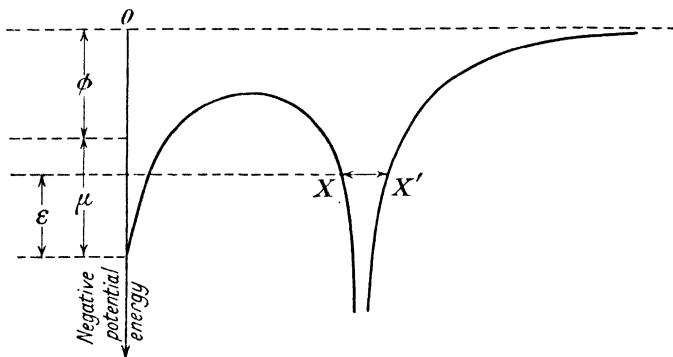


FIG. 13.—Liberation of Electrons from Metal Surfaces by Positive Ions (Oliphant and Moon).

very fast, it may approach correspondingly closely to the surface before undergoing neutralization, the height of the potential barrier here operative against the electron not being much reduced although its width will be lessened so that the ion is virtually in that part of the metal interface field due to the small work-function ϕ , and its capture of an electron is rendered more probable than before. In the extreme case when the ion is moving so rapidly that it reaches the actual metal lattice unchanged, the electrons are unhampered by any opposing influence and so can associate with the ion as easily as in free space, i.e. even those of zero energy may participate in the process. Finally, if V_i for the ion is less than ϕ , the extraction of an electron from the metal will be impossible, on thermodynamic and potential-barrier considerations alike, since according to the latter no electrons will be present of kinetic energy great enough to fit into any of the available energy levels of the ion; moreover, if

one did pass over, due to the tunnel effect, it could very easily return since in the metal there are vacant phase-cells of energy greater than μ . To this is due the very intense ionization observed when an alkali-metal vapour, e.g. potassium, is heated by a filament composed of some substance of high work-function, such as tungsten; when the voltage applied to such an electrode is high enough to overcome space-charge, the positive-ion current is remarkably constant, being limited only by the rate at which the atoms strike the hot surface [170, 171]. Ions thus produced will naturally be reflected unchanged from the surface of a metal whose work-function is more than the equivalent of V_i , as was actually observed by Oliphant and Moon [167]. Now since the electron capture will take place at ca. 10^{-7} cm. or less from the surface of its associated electron atmosphere, whereas the velocity of a slow ion is some 10^6 cm./sec., the excited atom resulting from the process will not, in all probability, radiate its potential energy (equivalent to $(V_i - \phi)$ as a maximum and to $(V_i - \phi - \mu)$ as a minimum) but lose it in a collision of the second kind, leading either to the formation of an intensely heated area of atomic dimensions or else to the ejection of another electron, the energy with which this last is emitted being given by $V_e = (V_i - \phi) - (\mu + \phi)$ with $V_{e(\min.)} = (V_i - \mu - 2\phi)$ and $V_{e(\max.)} = (V_i - 2\phi)$ as the minimum and maximum limits respectively. These predictions were remarkably well verified by experiment, helium ions and a well outgassed molybdenum target being used. Here $V_i = 24.5$ V, $\mu = 13.5$ V and $\phi = 4.3$ V, whence $V_{e(\min.)} = 2.4$ V and $V_{e(\max.)} = 15.9$ V as compared with the 2.5 and 15–17 V observed as the two limits.

When the ion is moving very rapidly, it may pass through the potential barrier and reach the surface or even underlying zones before it is neutralized. In this case, an excited atom of energy V_i will be formed, and an electron emitted from the metal due to the degradation of the energy of this atom in a collision of the second kind; the energy of the electron will here be given by:

$$V_{e(\min.)} = V_i - \mu - \phi \text{ and } V_{e(\max.)} = V_i - \phi.$$

This type of electron capture was also observed by Oliphant and Moon, the probability of ejection of an electron increasing to some 90 per cent for 5000 V ions; the sharp upper and lower limits to the velocity spectrum tend to disappear, due to the straggling of the slow electrons emitted from deep in the metal, or, possibly, to the onset of another mechanism of emission. Other studies of the phenomenon are listed in the Bibliography [207–211, 276].

Cathode Sputtering.

Disintegration of the electrodes used in glow discharge tubes is a very well-known phenomenon and often leads to a variety of troubles. For example, the yield of atomic hydrogen or oxygen may fall away to practically nothing after some hours' running due to the catalytic action of the trace of metal from the electrodes, and the author has found that if electrodes of copper or brass are used for the preparation of active nitrogen the tube may become completely poisoned after only a few minutes since the product here is so very susceptible to surface destruction by the metal concerned. Under carefully controlled conditions, the effect can be turned to good account and has been used for the preparation of high resistances, optical wedges, etc.; the author has made glass-chromium seals by first depositing sputtered platinum upon roughened glass, plating nickel upon this, and finally building up a thick chromium layer in the usual acid bath.

The phenomenon is by no means understood, and it appears very likely that there are several causes which may be operative according to the conditions of working, one of these certainly being intense local heating resulting from ion recombination in collisions of the second kind. The effect is in general confined to the cathode, and the mass of metal lost in unit time given approximately by $M = K(V_c - V_0)$ where V_c is the cathode fall and K and V_0 are constants depending upon the gas and the metal concerned [172, 173]. This implies zero loss when $V_c = V_0$, the latter having the dimensions of a voltage, and is in consonance with the observation that in thyratrons and other tubes where the cathode consists of an alkaline-earth oxide, no disintegration occurs unless a certain critical voltage is exceeded [174], while when the process has started the rate of loss is proportional to the difference in V_c and V_0 . In the absence of chemical action, K varies roughly as the fourth root of the atomic weight of the gas, and evidence is not lacking that it equals $K_1 A/B$, where K_1 is a constant characteristic of the gas, A is the atomic weight of the metal, and B is an integer which is occasionally equal to the valency and lies between 1 and 4 [175, 176]. It is supposed that sputtering is most frequently due to one of two causes, viz. evaporation consequent upon the formation of intensely hot foci of atomic dimensions, or the purely mechanical disintegration of the surface as a result of direct momentum transfers from the positive ions.

The former theory has been most extensively developed by von Hippel [177, 178] who derives the necessary heat from the energy

of the incident ions and on taking into account the thermal conductivity of the metal, the secondary electron emission, etc., obtains an equation which approximately satisfies the experimental data. The very large thermionic emission which might be expected from such regions of very high temperature, may, as Compton and Langmuir point out [166] be limited by the intense space-charge over the area concerned, and hence the actual number of electrons escaping is kept small; but it might also be anticipated that this would to a certain extent be offset by the partial annulment of the space-charge by the field of the positive ion and so the difficulty remains unsolved.

Oliphant and Moon have shown [167] that when 600 V potassium ions are projected on to targets of Al, Ni, and Pt, the retarding potential curve for the secondary electrons is exponential to the volt axis. When the results are plotted semi-logarithmically, a straight line is thus obtained, and from its slope the "temperature" of the electrons (which must be identical with the mean temperature of the zones from which they are emitted) may be calculated by use of the expression: $\text{Slope} = 11,600/T$, due to Langmuir and Mott-Smith [179]. The actual values thus obtained for T were $10,000^\circ\text{C}$. for Al, $30,000^\circ\text{C}$. for Ni, and $66,000$ for Pt, and it may be significant that this also represents the order in which the metals sputter; the thermal conductivity decreases, moreover, as we pass from Al to Pt, as would be demanded by the "hot-spot" theory.

Tanberg [180, 181] measured the pressure upon the cathode of a vacuum copper arc, and, on the assumption that this pressure was due to the recoil of metallic atoms undergoing evaporation, calculated a temperature of ca. $500,000^\circ\text{C}$. for their source. Compton [182] interprets the observation, however, as being consequent upon the departure, from the cathode surface, of atoms formed by ion-neutralization and retaining a small fraction of their kinetic energy acquired in the cathode potential fall, this theory necessitating only a limited and quite reasonable departure from unity as regards the accommodation coefficient of the ions. The suggestion appears to have been verified for helium ions incident upon molybdenum [183]. Berkeley and Mason [212], on the other hand, have determined the velocity of the vapour stream issuing from the cathode region of a vacuum arc between copper electrodes (*a*) from the energy received by a vane some 3 cm. in front of the cathode, as measured by the rise in temperature, and (*b*) the momentum imparted to the vane, when it was arranged as a modified Crookes radiometer, and find

that it is moving at ca. $2 \cdot 10^6$ cm./sec., in confirmation of Tanberg's data. The force of reaction upon the cathode of a mercury arc is also consistent with its being the source of atoms leaving with a velocity of the same order [213], and on the balance of evidence it is difficult to avoid the conclusion that in some cases, at any rate, the effects which are observed are best explained by the theory of thermal evaporation of the electrode [see also 214 and 216].

It is very difficult to estimate at all accurately the heating effects of positive ions upon an electrode. If the ion has negligible kinetic energy, then the energy which it can impart to the surface will be equal to $V_i - (n\phi - V_a + V_r + V_k)$, all quantities being expressed in electron-volts and n being the number of electrons set free, while V_r and V_k are respectively the fractions of V_i , which represent energy radiated and retained by the neutralized atom in the form of kinetic energy, and V_a is the heat of adsorption of the neutral atom on the metal concerned. Of these quantities, only V_i and $n\phi$ can at present be determined, and V_a is in particular bound up with the physical condition of the surface since it involves the accommodation coefficient and hence is likely to vary considerably from case to case.

Recent studies by Compton and van Voorhis [184, 215] show that the heating up of a cold tungsten cathode by 50 V ions in Ar, Ne, and He, is only 0.8, 0.65, and 0.43 of that to be expected from the product of (current to cathode).(voltage), conditions being so arranged that the ions do not degrade energy by impacts with other molecules: the very low fractions of the calculated watt-output as actually observed, are apparently due to the existence of a large $n\phi$ term in the above expression, together with an uncertain figure for the positive-ion current since to this must be added the secondary emission due to the influence of the metastable atoms here involved. The extensive investigations of Oliphant and Moon [167] do show, however, that very considerable heating effects may be expected at electrode surfaces as a result of ion-neutralization, especially when the excited atom thus produced has a nearby metastable level from which it cannot radiate, and this may well be the reason for Holst's observation [185] that sputtering occurs at a tungsten electrode with argon ions which have been accelerated through only 25 V, although he himself prefers the theory of direct momentum transfer in explanation of his discovery. Moreover, Johnson has shown [186] that the heating of filaments placed at various points along a positive ray beam is quantitatively in accord with that to be ex-

pected were the effects due to the impacts of excited atoms decaying exponentially with time, as in Wien's experiments for the determination of the mean life of such states [187], and in view of the very large energy set free in such processes it is clear that if such deactivation were localized by variations in the catalytic properties of the surface—which is almost certain to be the case—considerable evaporation would ensue.

Chemical action must also be of much greater import than is generally supposed. Recent work upon the common atomic gases and free radicals has shown that they all possess a very marked ability to react with metals either to form compounds of a more or less stable nature, or else to undergo catalytic reversion to the ordinary form in termolecular processes in which the third body is a metallic atom. Oxides and nitrides, to quote a case in point, tend to be highly exothermic, heats of formation of 100 to 200 K. cal/gm. mol. being quite common, and one must remember that the chemical clean-up which so often occurs when these gases are in use, and which can be detected by analysis of the sputtered electrode material, could lead to enough local heating to account at any rate for some of the loss from the poles. A definite chemical reaction of the cathode material and the surrounding gas appears to have been found by Duffield [188] in the case of short carbon arcs burning in air at atmospheric pressure. Here the number of carbon atoms lost agrees closely with one quarter of the number of current-equivalents passed, as would be expected—since carbon is quadrivalent—were an electrochemical oxidation taking place. Considerable nitride formation is also observed when an arc is maintained between iron poles in an atmosphere of nitrogen, probably due to interaction of active nitrogen and the metal in its exceptionally finely divided condition immediately after condensation of the vapour [189, 190]. When hydrogen is concerned, actual reaction of the gas and the metal is perhaps not so likely, although hydrides can apparently be formed by atomic hydrogen, but an even more probable cause of sputtering is the extreme ease with which these same atoms can recombine at a metallic surface, a phenomenon which is the origin of the pin-points of brilliant luminosity often seen in "Wood" tubes; these represent minute fragments of electrode material which are acting as the foci for atomic reassociation and hence receiving the energy which has to be dissipated in this very exothermic reaction ($2\text{H} \rightarrow \text{H}_2 + 105,000 \text{ cal.}$).

It is very probable that many of the anomalies observed in con-

nection with sparking potentials are due to adsorption of the gas at the electrode surfaces, which leads to differences in their physical conditions and hence affects such properties as their work-function, etc.; an alternating current discharge in hydrogen, for example, may not pass in one half cycle if the electrodes have previously been used for direct current discharges, owing to differential clean-up at the two poles. In general, the cathode tends to adsorb the gas, and the anode to emit it, at rates which are functions of the currents, gas pressure, nature of the metals used, etc., and it is clear that such effects must also influence the extent to which they sputter [217].

Sputtering is almost invariably accompanied by fracture of the crystalline surface layer of the electrode concerned [191, 192], and the material ejected generally consists of neutral atoms which travel with the velocities common in low-pressure, high-temperature evaporation processes [191, 193, 275] although charged bodies may be formed later owing to the electric fields present, and lead to aggregation, etc., as in a Cottrell precipitator. Moreover, the distribution of sputtered metal in the inter-electrode space suggests that the atoms diffuse away from the region of maximum concentration near to the cathode towards the anode zone where their partial pressure is negligible [194], but this need not of necessity be regarded as proof of the thermal evaporation theory, since, as Compton and Langmuir point out [166] it might well be due to the initial production, by mechanical disintegration, of a dust whose particles are of atomic magnitude and undergo subsequent vaporization through acting as foci of the strongly exothermic recombination of electrons and positive ions.

Very considerable differences are found, both as regards manner and degree of sputtering, as we pass from a homogeneous material to one which is covered with another substance, as is shown in Fig. 14; the first of these represents the behaviour of pure tungsten [195], while the second refers to the loss of surface atoms from a tungsten filament covered with a monatomic layer of thorium [196, 197]. Both were obtained with very low pressures of gas, so that the velocity with which the ions strike the target can be accurately computed from the accelerating potential applied to the tube. In the first case the simple expression given on p. 60 is followed, except that V_0 is much lower than is found in glow discharges, indicating, according to Compton and Langmuir [240] inaccurate values for the velocity with which the ions strike the electrode since at the higher

pressures they will lose, by collisions, much of the energy which they acquire in the cathode field.

To explain the second case, Kingdon and Langmuir [196, 197] adopt the theory of direct momentum transfers as the cause of sputtering. They suppose that surface atoms of thorium are driven into the underlying tungsten by impact of the ions, and then become able to reflect elastically further charged bodies which may strike them; if one of these latter moving away from the surface collides with another thorium atom, then, provided that its available energy, according to the laws of momentum transfer, exceeds the

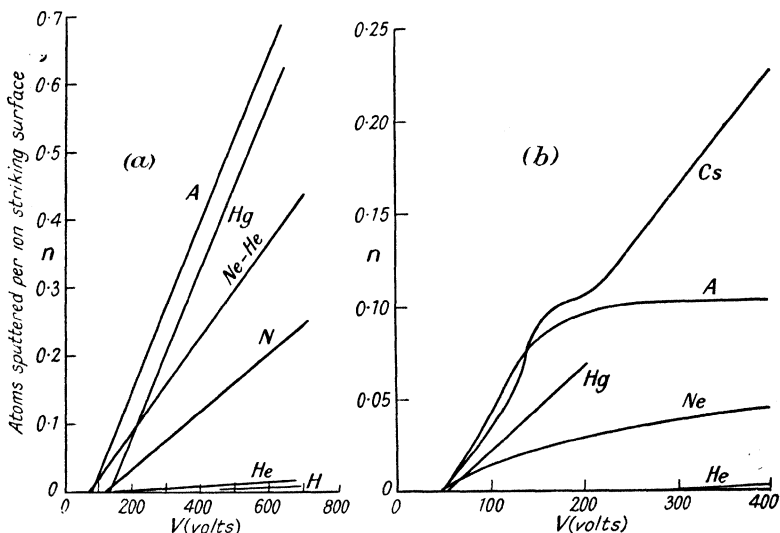


FIG. 14.—Sputtering of (a) pure and (b) thoriated tungsten (Compton and Langmuir).

atomic heat of evaporation of the adsorbed layer, it may remove the atom concerned. The fraction of the surface covered by thorium atoms being known, and reasonable values being assumed for the probability that a given ion will strike a given atom and that a reflected ion will dislodge an atom as the theory demands, an expression can be derived which quite accurately fits the data for the rate of sputtering and approximately predicts the minimum voltage at which loss of the thorium will set in; in the latter case, the critical potential V_k is given by:

$$V_k = \frac{300E_v}{4em_1m_2} \left[\frac{(m_1 + m_2)^2}{m_1 - m_2} \right]^2$$

where E_v is the atomic heat of evaporation of thorium from tungsten (1.41×10^{-11} ergs/atom), and m_1 and m_2 are the masses of the ion and the thorium atom respectively. The values V_k as calculated and observed are in fair agreement for Ne and Ar, but much too high for H, He, Cs, and Hg ions. In the case of hydrogen and helium, the anomaly is attributed to the very high penetrating power of the ions, which causes the effect to take place so deep in the metal that it does not become manifest at the surface; it will be remembered that Oliphant and Moon [167] showed that He^+ can pass well into the main mass of a target and in consequence cause the emission of very slow electrons, so that this view seems quite reasonable. The heavy ions Cs^+ and Hg^+ , on the other hand, drive the thorium atoms so far into the supporting metal that ions reflected from them in subsequent encounters have to emerge through a passage lined with tungsten atoms, as it were, and hence the sputtering proceeds very much as if the surface layer were absent and pure tungsten only were concerned. It is a consequence of this theory, that, since momentum transfers are involved, the rate of sputtering should vary with the angle of incidence of the ionic beam with regard to the cathode, and it would be of interest to study these factors simultaneously with the secondary electron emission and the usual thermionic properties of the electrode; such an investigation would clearly provide data to help in deciding between the two main possible causes of sputtering.

The theory also necessitates a close relation between the sputtering and the physical nature of the surface, and Johnson [198] in a very interesting paper, has recently shown that this is the case. The exceptionally violent bombardment of the cathode which occurs when a discharge is passed in a gas capable of multiple ionization has been postulated by Thomson [199] as the primary cause of sputtering, but Johnson finds that with aluminium an abnormal rate of loss of electrode material persists even after all traces of the particular gas (in his experiments, mercury vapour) have been removed by prolonged pumping and baking-out. The effect appears rather to be due to the partial disintegration of the protective layer of oxide with which aluminium is almost invariably covered, leading to a weakening of the metallic structure and hence greater ease of fracture and sputtering. It also facilitates the diffusion of dissolved gases from deep within the metal and can account for the apparent transformation of Al_2O_3 and AlN into hydrogen when a discharge is passed between aluminium electrodes in the

presence of helium and other noble gases, as observed by Baly [200].

Desorption of Gases from Solids under Impact of Metastable Atoms.

A discovery has recently been made by Johnson [201] which may be of much importance in explaining the irregularities, such as softening, which are sometimes very troublesome in lamps, valves and other forms of discharge tubes, and is clearly related to one of the forms of sputtering discussed above.

When pure hydrogen is subjected to an electrodeless discharge in a very well baked-out silica bulb, the fall in pressure which occurs is consistent with the formation of a unimolecular layer of atoms [202, 203] as in the original experiments made by Langmuir [204], the surface density of the film corresponding to very nearly the maximum theoretical packing.

In a mixture of hydrogen and mercury vapour irradiated by the full light from a cooled mercury tube, the initial pressure fall due to adsorption of the products of dissociation becomes constant when the same unimolecular layer is formed, but with only one-quarter of the former surface-density. A liberation of gas then commences, independent of the partial pressure of hydrogen, but controlled by the pressure of the mercury and the absorption of the resonance radiation. It appears very probable that one of the constituents of the film in this case is the unstable mercury hydride which can be detected in Cario-Franck experiments, while the desorption is due partly to the decomposition of this layer and partly to emission of gas from the silica consequent upon the deactivation of excited mercury atoms at the surface; since the heating here would be confined to a zone of atomic dimensions, the effect upon the quartz would completely transcend that of even the hottest blowpipe flame used for ordinary baking-out and much further diffusion of gas from the interior should follow.

Although the magnitude of the effect is not very great, it might become of much importance in some types of photochemical work when traces of foreign gases are of account, as in the interaction of hydrogen and chlorine. Moreover, in discharge tubes filled with the noble gases and others which possess metastable levels, a gradual and quite unsuspected contamination might occur. The present author has in his possession a triode containing mercury vapour which showed only the spectrum of this metal when new, but now, after some two and a half years' use, gives strong emission due to

nitrogen and argon, especially the latter ; the effect does not seem attributable to a leak, since there is no evidence of oxygen or any mercury oxide, which rapidly forms "tailings" in such a case ; and it may well be that the effect is due to a process such as that described above.

CHAPTER V

THE QUENCHING OF RESONANCE RADIATION

It has been known for many years that both the intensity and the nature of the resonance radiation from an emitter which is being stimulated in the presence of other gases or vapours may differ in a marked degree from that where the pure substance only is concerned; the pioneer work upon this subject, due mainly to Wood, is described with a wealth of detail in Chapter XX of his "Physical Optics." The phenomenon was first successfully explained by Franck's generalized theory of collisions of the second kind, but in its quantitative aspects there is still some obscurity since later work has shown that the diluent acts not only upon the photo-excited bodies *per se* but also very probably influences their genesis as well owing to broadening of the spectral lines in the primary radiation. So far, the majority of the studies upon this quenching effect have been made with mercury vapour, which is in one way unfortunate since the interpretation of the data is rendered more difficult by reason of the existence of a metastable level close to the usual photoexcited state; but it has the advantage of being very easily handled and hence has provided a mass of information which is of the greatest value and can be applied to other cases after due allowance has been made for the peculiarity just mentioned.

We shall first consider the broadening of spectral lines as it may arise in various instances.

Doppler Broadening.

According to Doppler's principle, the frequency of an oscillation as received depends upon the translatory velocity of the emitter, with respect to the observer, and this, for electromagnetic radiation may be expressed by $\nu = \nu_0 (1 + \frac{v}{c} \cos \theta)$ where ν and ν_0 are the frequencies as received and transmitted, v is the velocity concerned, and θ is the angle between the lines of motion of the oscillator and that along which the measurement is made.

For a luminescent vapour where the molecules are moving

directionally at random but with a Maxwellian distribution of velocities, this Doppler effect, on classical and quantum principles alike, results in a symmetrical widening of a spectral line about the "true" position, the so-called "Doppler half-width" being given by: $\Delta\lambda/\lambda = 3.58 \times 10^{-7} \sqrt{T/M}$. To this is due the diffuseness often found in arc spectra, etc., and the principle has been used with much success to determine the velocity and temperature of emitters under very varied conditions, e.g. its application by Wien for the evaluation of molecular velocities in his method for determining the duration of the excited state. The Doppler broadening is not of much importance in the rather general treatment adopted here, except where the source of the radiation is a metal of high boiling-point, and other influences which produce the same effect are of greater moment. It has, however, interesting consequences in some photochemical reactions such as the dissociation of NaI [113]. This occurs with only a small degree of resonance when light in the ultra-violet region is used, the energy discrepancy going at first into exciting the sodium D lines and, as the wavelength of the excitatory radiation is decreased, into raising the velocity of separation of the Na and I atoms, so that the Doppler broadening of the fluorescent lines leads to a marked diminution in their ability to absorb other D lines from an ordinary low-temperature source.

Natural or Ladenburg Broadening.

These considerations were first worked out by Voigt [220] and Reiche [221] nearly twenty years ago, in connection with the absorption coefficient of a gas as it is related to the Doppler effect, and various other influences which can be correlated with the velocity of the atoms therein. The greater part of the recent work along these lines has been done by Ladenburg and his associates, and it seems appropriate that the effect should bear his name. Briefly, it may be stated that the "natural" breadth of a line $\Delta\nu_N$ is related to the Einstein A coefficient and the free life period of the oscillator by: $\Delta\nu_N = A/(2\pi) = 1/(2\pi\tau)$.

Combining the natural and the Doppler broadening effects, it may be shown that when the absorption is weak the absorption coefficient is determined by the magnitude of the latter, but when it is strong the former predominates. It may be mentioned that the Doppler broadening seldom exceeds some hundredths of an Ångström Unit, and the "natural" broadening is in general even smaller.

The Stark Effect.

Allusion has already been made (p. 33) to shifts in normal series limits induced by Stark interaction among atoms of the same kind. This same process may also cause some broadening of absorption lines, but it is so far very difficult to assess its magnitude in comparison with other causes which lead to the same effect.

The Holtsmark Effect.

This is the broadening of an absorption line which accompanies an increase in the pressure of the absorbing material in the absence of foreign gases. It was first treated theoretically by Holtsmark according to classical principles [223] but later investigations suggest that the original assumptions were incorrect and that in all probability it is to be regarded as a special case of the commoner Lorentz broadening [222].

Lorentz Broadening.

This, and the Holtsmark effect just mentioned, are very often grouped together as "pressure broadening," and at any rate in some cases, appear to constitute one of the major obstacles towards a simple interpretation of the quantitative data upon the quenching of resonance radiation by foreign gases (cf. 266, 267).

Lorentz [224], accepting the common assumption that perturbing collisions are the cause of the broadening of the spectral lines which accompanies an increase in the pressure of the absorbing gas, estimated the intensity distribution and the half-width of the line according as the effect arose from impacts of the absorbing atoms either among themselves or with foreign molecules present, but was not able to provide for the case where the two kinds of interaction occur simultaneously. The general line of reasoning here adopted is, that when the atomic oscillator is permitted to absorb or radiate freely, it will emit a train of waves which can be shown, by a Fourier analysis, to correspond to a single line; but when it suffers collisions in the process, the train will be broken up into a series of components and hence the radiation will no longer be strictly monochromatic. His theory cannot, however, explain either the development of asymmetry or the shift in the position of maximum intensity of the absorption line, and it is only recently that Weisskopf [222] has given a satisfactory interpretation of these phenomena in general. As in the well-known case where the kinetic energy of the nuclei of a diatomic molecule can provide a positive or negative increment to the electron terms, so, according to Weisskopf, can the translational energy of the atom combine with its internal

energy acquired through optical absorption. But since in the latter case we have to deal not with quantized terms but with unordered heat energy, what is virtually a continuous spectrum becomes superimposed upon the original line, the whole effect constituting a very interesting example of the principle of microscopic reversibility. Its classical analogue is the Lenz perturbation wherein the phases of the normal vibration of an oscillator are altered by the approach of another body [225], this last investigator having improved upon Weisskopf's theory as first stated [226] so that now there is a very good agreement between the observed and the predicted appearance of the lines concerned.

The broadening of a spectral line in the presence of foreign gases

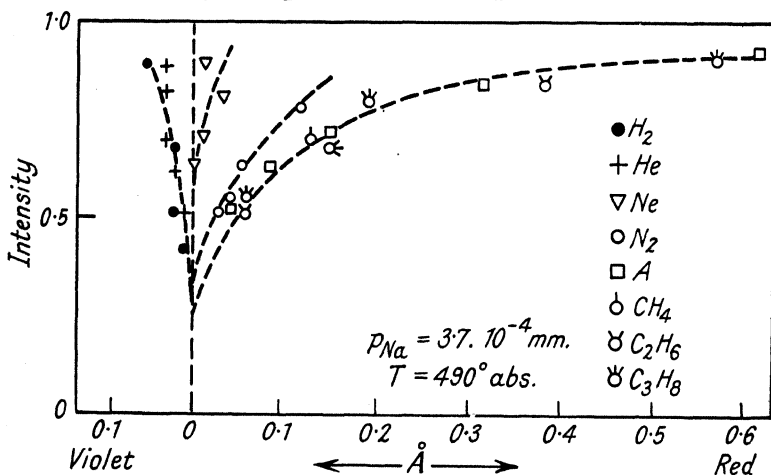


FIG. 15.—Pressure Broadening of the Sodium D Lines (Minkowski).

is accompanied, as has long been known, by the development of an asymmetry of intensity about the "true" centre of the line. The phenomenon has been extensively studied, notably by Füchtbauer and his school [e.g. 344-347], and it appears that the "half-width" increases proportionally with the density of the diluent material whereas the Stark broadening increases more nearly as the four-thirds power of the same constant. Moreover, the asymmetry becomes more pronounced towards the red as the molecular weight rises, as is shown in Fig. 15, given by Minkowski [343] for the pressure broadening of the sodium D lines at 490° K , with $3.7 \times 10^{-4} \text{ mm.}$, of the vapour, and 93 mm. , of diluent; the distances along the abscissa refer to the centre of the line as zero. Minkowski

regards the effects as due to the interaction of kinetic and radiational energy on much the same lines as those later, and more precisely, developed by Weisskopf [222] and Lenz [226]. (An excellent discussion upon these and related phenomena is given in Vol. XXI of the "Handbuch der Physik.")

Reactions with Mercury Vapour and the Difficulties of Metrical Study upon Quenching.

If now mercury vapour be illuminated in the presence of another gas, by the resonance line $\lambda = 2537$, two effects may be anticipated, viz. : (a) an increase in the intensity of the fluorescence due to enhanced absorption following pressure broadening of the incident line, and (b) a diminution arising out of deactivation of the excited atoms in collisions of the second kind. This is well illustrated by an early observation, due to Wood [106, 107], that addition of helium or argon to mercury increases the intensity of resonance emission whereas hydrogen or air under the same circumstances lowers it very considerably ; in the first case, effect (a) is manifest—although the formation of large numbers of 2^3P_0 atoms must not be left out of account—while in the second, (b) is predominant. Numerous attempts have been made to study these processes from a quantitative standpoint, but it is by no means clear as to how much validity can be attached to the results so far extant, with certain exceptions.

Stuart [108], using better experimental conditions than those adopted by Cario [112] and Cario and Franck [125, 126] and Turner [110] who were among the first to carry out such studies, excited $\lambda = 2537$ by illuminating pure mercury vapour with the narrow line from a water-cooled lamp, and then led the resonance beam through a half-silvered slide so that part fell directly upon a photographic plate while the other passed first through a vessel containing mercury vapour together with the gas under examination ; in this way the conditions of emission of the resonance line were kept constant, while any variation in the source could also be allowed for. Very considerable differences in the behaviour of the different gases were found, as Table 7, taken from Stuart's paper, shows.

The quantities $P_{\frac{1}{2}}$ and $t_{\frac{1}{2}}$ represent respectively the pressure of the diluent gas and the time interval between collisions at which the intensity of the resonance radiation is reduced to one-half of its value in the absence of the foreign molecules, and are introduced since, in calculating his results, Stuart employs an equation due to Stern and Volmer [111], i.e. at the point when the above condition

is attained, the fraction of impacts between an excited atom and the other bodies which lead to deactivation of the former, is expressed by $x = t_i/\tau = 1/\tau Z$; Z is here the number of collisions suffered by a particular atom and is evaluated from the formula

$$Z = 2(\sigma_1 + \sigma_2)^2 n \sqrt{\frac{2\pi R\tau(M_1 + M_2)}{M_1 + M_2}}$$

where n_1 , σ_1 , and M_1 refer to the molecules of the diluent gas and σ_2 and M_2 to the mercury atoms, and τ is the average life period of the excited atom.

TABLE 7

| Gas. | P_i . | t_i . | = Deactivation. |
|---------------------|----------------|---------------------|-----------------|
| Hydrogen | 0.2 | $7 \cdot 10^{-8}$ | 70 |
| Oxygen | 0.35 | $1 \cdot 10^{-7}$ | 100 |
| Carbon Monoxide . . | 0.4 | $8 \cdot 10^{-8}$ | 80 |
| Carbon Dioxide . . | 2.0 | $2 \cdot 10^{-8}$ | 20 |
| Water Vapour . . . | 4.0 | $1 \cdot 10^{-8}$ | 10 |
| Nitrogen | 30 | $1.3 \cdot 10^{-9}$ | 1.3 |
| Argon | 240 | $2 \cdot 10^{-10}$ | 0.2 |
| Helium | 760 | $3 \cdot 10^{-11}$ | 0.03 |
| | (Extrapolated) | | |
| Air | 1.2 | | |

Studies on much the same lines, with various experimental modifications, have been made by Mannkopf for sodium [115] and by Bender for cadmium vapours [116].

The interpretation of the quantitative aspects of these, and similar observations obtained with other vapours such as iodine, is a matter of much difficulty and the authorities are by no means in agreement upon many interesting points. We shall not seek to deal comprehensively with the subject here, since it is beyond the scope of this book and in any case has received an exhaustive description by Mitchell and Zemansky [256] to whom—the latter especially—we owe so much of the experimental work. As an example, however, we may discuss representative papers by Zemansky [312] and Foote [313]. (The early work has been admirably summarized by Bates [249].) Stuart himself realized that the adoption of the ordinary “kinetic” diameter for the excited mercury atom would, if taken along with the Stern-Volmer condition for the resonance radiation being reduced to one half when the

chance that an excited mercury atom will radiate equals the probability that it will undergo a deactivating collision with a foreign gas molecule, necessitate the assumption that τ , the duration of the excited state, is much larger than the value 10^{-7} sec. found by several concordant methods [see 314]. The least value for τ in any one case will clearly be obtained when x is unity, i.e. at its maximum, and any decrease in x will merely raise τ still farther. If, on the other hand, as appears less objectionable, we adopt the accepted value for τ , the effective cross-section of the mercury atom towards the diluent becomes much larger than that generally found, and, from Stuart's figures, works out at $6 \cdot 10^{-8}$ cm., the usual diameter being $1 \cdot 76 \cdot 10^{-8}$ cm. [see also 115].*

Moreover, Stuart also assumed that only those impacts which led to diminution of the resonance radiation were collisions of the second kind, and from his quenching curves, using the abnormal cross-section of the excited mercury atom, calculated efficiencies—i.e. the likelihood of a collision being one of the second kind—of 100 per cent for oxygen, 70 per cent for hydrogen, and lower values, down to 0.03 per cent for helium, with the other gases. (It is not

* A digression upon a matter of terminology would here seem desirable. We must be careful as to the exact significance attached to the term "diameter." In all cases, no matter how it is measured, what is ultimately evaluated is the distance to which two molecules can approach before they begin to affect each other *to an extent large enough to be detected by the technique employed*, and when, as in these cases, we have to deal with bodies in an abnormal condition due to excitation, a certain deviation from the normal may be expected both in the manner and degree to which they interact; even upon the older quantum theory the cross-section of an atom increases with excitation. In fact, the term "diameter" is quite without meaning in molecular processes unless one specifies the reactions to which it is to be applied. Towards an α -particle, the diameter of an atom is virtually that of its nucleus, as the classical scattering experiments of Rutherford demonstrate [see 304]. The Ramsauer effect [253–255] shows the abnormally high cross-sections of molecules towards slow electrons within a certain range of velocities, while in collisions of the second kind the effective cross-sections are apparently greatest when there is the maximum energy-resonance (and probably conservation of spin momentum as well) between the systems concerned [269]: this last is particularly well demonstrated by the depolarization, by sodium itself, of the sodium D lines developed by fluorescence [270, 271] and the same great excess of σ over the usual "gas-kinetic" value is mentioned in several other places in this book. Wave-mechanical theory, it may be mentioned, quite demolishes all the classical pictures of impacts, since bodies can, we are assured, "collide" at even infinitely large separation. Perhaps the ordinary scientific worker may here be justified in adopting a certain measure of philosophic doubt towards the conclusions of our new prophets! [cf. 109].

now possible to suppose, as did Zemansky, that the close resonance between the energy of the excited mercury and the heat of dissociation of hydrogen should confer a 100 per cent quenching efficiency upon the latter gas, with more than 100 per cent for oxygen in consequence. The resonance, although good—especially for the 2^3P_0 state—is not *very* close, and studies such as those of Beutler and Josephy [40] show how great may be the influence of even a small energy discrepancy in this connection.) Foote, on the other hand, assumed that *all* impacts between excited mercury atoms and foreign molecules were collisions of the second kind, but that only in the case of hydrogen does the former pass completely to the ground state with entire utilization of its energy in dissociation of the gas, which thus appears to have the 100 per cent efficiency mentioned. Other gases, and unexcited mercury atoms, also, were supposed merely to transfer the 2^3P_1 atoms to the lower metastable state, which then undergoes collisional re-excitation to the upper level, while another probability, also investigated, was the reabsorption of $\lambda = 2537$ emitted by the primarily excited species. This theory would necessitate a quenching efficiency of > 100 per cent for oxygen, a point not dealt with by Foote, and Zemansky therefore extends the range of possible fates of the excited atom by taking into account the imprisonment of resonance radiation, which is known to occur in such cases.

Imprisonment of Resonance Radiation and Surface Effects in Quenching Phenomena.

This last factor was first considered by Milne [315] and is simple as regards its fundamentals although requiring very complicated mathematical treatment for its full development. Since a process: $A + h\nu \rightarrow A'$ (where A' denotes a photoexcited state of an atom A) is reversible, it is an *a priori* consequence that the photon emitted in the return of A' to the normal state will have a poor chance of escaping from the system because of reabsorption by other A 's. Hence it will undergo a prolonged journey among the atoms—an ethereal van der Decken—until wall deactivation of its temporary abode,* or a fortunate spatial distribution of its would-be captors,

* Destruction of 2^3P_1 atoms at the surface cannot be very pronounced, although it must not be neglected. The velocity of a mercury atom at 20°C . is ca. $2 \cdot 10^4$ cm./sec., and since the lifetime of the excited state is ca. 10^{-7} sec. only those atoms in a layer 10^{-3} cm. from the wall will have even a chance to be deactivated. Radiation, on the other hand, may escape if the source is ca. 0.2 cm. from the wall in a gas where mercury is present at a pressure of 0.001 mm., the saturation value at the above temperature.

either transmutes it into kinetic energy or else sets it free into space. (An account of the phenomenon, with special reference to this particular application of Milne's theory, is given by Mitchell and Zemansky [256].) Taking into account the geometry of Stuart's apparatus, and making only one assumption as to the behaviour of the diluent molecules, i.e. that the number of collisions of the second kind per c.c. is proportional to the concentration of excited mercury atoms, the proportionality factor k being an unknown function of the pressure of the foreign gas, Zemansky was able to show that the quenching efficiencies of the various gases vary with their pressures if τ be assumed constant, or that σ similarly depends upon the pressure if τ be regarded as invariable, so that the common assumption as to the number of quenching impacts bearing a fixed ratio to the total number of collisions, is not justified. This anomaly could, however, be explained by the use of another deduction, viz. that the only place where any large formation of excited atoms occurs is close to the face of the apparatus whereupon the light is incident. Putting n = concentration of excited atoms per c.c., the quantity $nk\tau$ represents the number of times in 10^{-7} sec. that the atoms give up their energy to the foreign molecules and hence the rate of change of condition of the latter, i.e. the reaction velocity, and this, plotted logarithmically against the gas pressure p , gives a family of straight lines of nearly constant slope = 0.6. The reaction velocity thus varies as $p^{0.6}$, *independently of the nature of the gas concerned*.

This was supposed to mean that there is here not a volume reaction of the kind usually envisaged, but a heterogeneous process, since the "order" is not given by an integer but by a fractional number 0.6. Now it is known that the metastable atoms which are produced by the action of some diluent gases upon photoexcited mercury have very long life periods [154, 278], so that it should be easy for the surface to become covered, according to Zemansky, with an adsorbed film composed partly of metastable atoms and partly of gas molecules, and if the concentration of the former were not large enough to saturate the walls, then the amount of the latter held there would vary as a fractional power of the pressure, according to the Langmuir adsorption isotherm. Hence at equilibrium the rate of arrival of metastable atoms at the wall would equal the rate at which the foreign gas molecules are activated, which in turn would depend upon the fraction of the surface covered by them; hence the pressure relations observed in Stuart's experi-

ments when recalculated in this manner. It is also significant, as pointed out by Zemansky, that other studies [118, 315] upon the clean-up of hydrogen and oxygen in such Cario-Franck experiments in the presence of nitrogen and argon, added to enhance the concentration of metastable atoms of mercury, show a reaction of zero order; under these conditions the walls are regarded as saturated, which, upon the mechanism considered here, would mean that the concentration of 2^3P_0 atoms is large enough to cover the whole of the surface so that none is left to accommodate the hydrogen or oxygen, as the case may be. There are various difficulties connected with this ingenious theory—the author himself does not stress it in later publications—and it is unfortunate that there is little or no evidence available upon the kinetics of heterogeneous photochemical reactions to assist in an estimation as to the validity of Zemansky's conclusions. For one thing, one cannot be certain that the adsorbed metastable atoms would have any appreciable life upon the walls, since there is much reason for believing that surfaces are, in general, highly destructive towards such bodies (see Chapter IV), and they might easily be eliminated in a process whereby an electron is emitted rather than in reaction with a gas molecule. His suggestions are, however, of much value in illustrating the numerous variables which have to be taken into account in work of this kind, as well as the pitfalls before the experimenter who seeks a simple explanation of his results [cf. 348]. It may, however, be of interest to recall definite experimental observations which indicate that surface phenomena will very probably prove of importance in some classes of photochemical investigation. Bonhoeffer has shown [86] that many substances fluoresce brilliantly when placed in a stream of atomic hydrogen from a Wood tube, this being in part due to chemical reaction and yet again—especially in the case of the metallic vapours—to excitation through their acting as the third body in the termolecular recombination of the atoms (p. 23). Liquid mercury at room temperature becomes covered with a blue flame whose spectrum shows a strong development of both the mercury resonance line at $\lambda = 2537 \text{ \AA}$, and bands extending from ca. $\lambda = 5000 \text{ \AA}$ towards the shorter wavelengths which are due, according to Hulthen [316], to mercury hydride, HgH ; some of the Hg_2 continuum in the green was also seen. (A number of references to the spectroscopy of these bands are given in the paper.) All attempts to obtain the bands and the resonance line independently of each other or with vaporized mercury were

unsuccessful, the effect being observed only at the surface of the metal; when this was boiling, the luminescence vanished, since the hydrogen atoms could not diffuse against the emergent vapour. Since the heat of dissociation of hydrogen is now known to be 4.4 V, whereas the line $\lambda = 2537 \text{ \AA}$ corresponds to 4.88 V, the non-appearance of the latter in the homogeneous reaction is easily explained, but the development of the hydride bands is more difficult to account for. Cumulative excitation might be invoked to account for the appearance of both the line and the HgH bands, but the absence of more experimental data and some uncertainties as to the heats of formation of the hydride render further conclusions very speculative. There are also the curious results obtained by Hirst [330], who found a number of photochemical reactions to take place with great ease at a mercury surface illuminated by the full radiation from a mercury arc, whereas, in the absence of the liquid metal they occurred either not at all or else with great reluctance. Since the processes studied were all hydrogenations, there is a natural suspicion that mercury hydride may have been involved, although other possibilities must not be neglected, e.g. that the mercury was chemically consumed, so that a supply of the liquid metal was essential to maintain a concentration of vapour adequate for reaction in the gas phase.

We may thus summarize the considerations given in the preceding pages by stating that the obstacles to the quantitative interpretation of quenching of resonance radiation are:

(a) Pressure broadening, either as a Holtsmark or Lorentz effect, or both.

(b) Diffusion of imprisoned resonance radiation.

(c) In mercury in particular, the existence of the metastable state close to the usual photoexcited one, and the undoubted formation of a hydride.

(d) Wall effects—which are probably connected with (b).

(e) Chemical interaction of the excited atoms and the foreign gas.

(f) The resonance and spin-conservation rules.

As regards (a), it would appear not unlikely that it may be the cause of Zemansky's conclusions (*supra*) as to the quenching powers of all the gases used by Stuart acting proportionally to the 0.6 power of their pressure. On the other hand, one feels a certain reluctance to suppose that pressure broadening can be of such importance when we consider that for measurement upon the Lorentz effect, gases generally have to be used at a pressure of

many atmospheres. It would appear that broadening of the incident line cannot always be of much importance, since recent experiments by Melville [257] have failed to show effects of the kind anticipated when this condition obtains. If broadening were entirely absent, then the rate of dissociation of NH_3 and ND_3 should be given, for the mercury sensitized photochemical reaction, by an equation of the form :

$$1/R = 1/R_{\infty} \cdot (1 + A/[\text{NH}_3])$$

where A is a factor dependent on the velocity coefficient for collisions between excited mercury atoms and NH_3 or ND_3 molecules and also upon the mean life of the excited atom ; R_{∞} is the rate when the concentration of ammonia $[\text{NH}_3] = \infty$. Hence the plot of $1/R$ against $1/[\text{NH}_3]$ should give a straight line with a finite intercept $1/R_{\infty}$ on the $1/R$ axis, whereas were broadening present, the line should become concave to the $1/[\text{NH}_3]$ axis. With a lamp known to give a fairly broad line, no such deviation can be detected—to within at least 10 per cent—even at 500 mm. pressure, whence it must be concluded that unless some compensating influence acting perfectly in accord with the gas pressure is operative, then any broadening effects which may occur are of small moment compared with other factors. A similar conclusion was reached by Foote [313] some time ago, although direct evidence upon the point was not then available.

For discussions upon (b) the reader is referred to the authorities, while items (c), (d), (e), and (f) are discussed either in the following pages or in other parts of this book. At present, it would appear advisable to suspend judgment upon the metrical aspects of the subject, and, where quenching curves are to be considered, regard them as giving only a measure of the *relative* abilities of the various gases in this connection, bearing in mind that the magnitude of each of these disturbing influences is certain to alter from case to case, so that a perfectly generalized theorem is, in all probability, unattainable.* It will therefore be understood that the subsequent

* Some authorities [e.g. 380] consider that of all the numerous methods for the determination of absolute values for quenching radii, etc., that least open to objection is based upon the optical dissociation of metallic halides to one unexcited and one excited atom. Sodium iodide, for example, breaks up [378] under the action of $\lambda = 2430 \text{ \AA}$: $\text{NaI} + h\nu(\lambda = 2430) \rightarrow \text{I} + \text{Na}(3^2\text{P})$, which means that the fluorescent atom is produced and excited in one act under conditions where, by proper attention to temperature control, diffusion of resonance radiation and pressure broadening by atoms of the same kind can be disregarded. Moreover, since any energy discrepancy goes into en-

allusions to quenching relate to qualitative data only, without prejudice as to the extent wherein future quantitative investigations may necessitate a modification of the views expressed.

A Possible Classification of Gases as Quenching Agents.

As a tentative codification of the behaviour of various gases and vapours upon resonance fluorescence, we may divide the effects into two main classes. Although the suggestions are here given with special reference to mercury, they seem equally applicable to other cases as well, provided that certain obvious modifications are made.

In the first, the chemical composition of the system remains sensibly unchanged throughout, and hence the interaction of the diluent and the excited mercury atom may formally be regarded as a purely physical process in which the foreign molecule merely acts as a carrier for the energy which is transferred. In this category we may place the noble gases, nitrogen, and carbon monoxide.

As regards the second, a chemical change is definitely traceable and results either from combination of the excited mercury and the diluent gas (as, for example, with oxygen) or else from decomposition of the latter—with or without secondary reactions—upon receipt of whatever energy is handed to it upon collision. The dissociation of hydrogen, and the production of formaldehyde, accompanied by some polymerization, from hydrogen and carbon monoxide, exemplify this class of reaction.

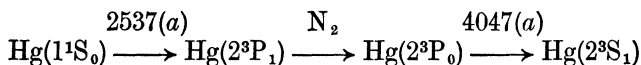
Both types of effect are, however, often simultaneously operative, and hence for this reason alone considerable care is essential in the interpretation of the results of an experiment. The border line between a "physical" and "chemical" process is in any case very arbitrary, the only real difference being that the latter exhibits a certain degree of non-reversibility under the conditions of the experiment concerned. However, for the first of these classes the following principles seem of general validity, although occasional exceptions are known.

(a) The monatomic noble gases (e.g. He, Ar) whose lowest electronic levels are much above that of the excited mercury, energetically speaking, have but little effect upon the resonance radiation because of their inability to react appreciably with the emitter

hancement of the kinetic energies of the atoms [see 113, 379] it becomes possible to superpose, at will, a known Doppler broadening by the use of light of wavelength $< \lambda = 2430$, and thus study an important variable under precisely defined conditions.

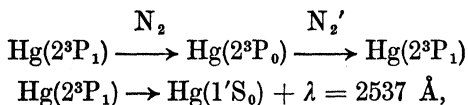
concerned. At most, they seem able only to induce the $2^3P_1 \rightarrow 2^3P_0$ transition, which involves a loss of 0.218 V as kinetic energy. The polyatomic gases, on the other hand, have many vibrational and rotational levels in which the energy can be taken up, there is no need for the interchange to involve a single-step degradation of the electronic energy of the mercury atom into *vis viva*, and hence they have a considerable damping effect upon the fluorescence. Nitrogen is apparently anomalous in this respect, but its behaviour will be discussed later.

(b) In mercury in particular, the situation is complicated by the existence of the metastable 2^3P_0 level which lies only 0.218 V below the photoexcited state. Although it appears that the latter would, if left to itself, tend to pass to the 1^1S_0 ground state with emission of $\lambda = 2537 \text{ \AA}$, some substances can induce the $2^3P_1 \rightarrow 2^3P_0$ transition and hence although they do in one respect quench the fluorescence, they leave the mercury atom in a condition in which it can very easily be re-excited and then radiate. For example, Wood has found that mercury at ordinary temperatures, either alone or mixed with nitrogen will not absorb $\lambda = 4047 \text{ \AA}$, for which the metastable level is the basic term, unless $\lambda = 2537$ is also present in the excitatory radiation: this is clearly to be explained by the successive reactions:



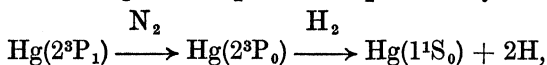
The effect is parallel to that observed for the two D lines in sodium (pp. 31, 32).

It has also been found [117, 118] that while the quenching effect of hydrogen is the same at 750° as at 18°C ., nitrogen has practically no effect at the higher temperatures, most probably due to the consecutive reactions:



where N_2' connotes a nitrogen molecule of high kinetic energy. The fraction of molecules of the diluent gas having an energy in excess of the 4600 cal. difference in the 2^3P_1 and 2^3P_0 states being ca. 10^{-1} under these conditions, there is clearly every chance that reactivation will occur. The addition of a small amount of nitrogen to hydrogen in this case markedly enhances the quenching power of the latter gas, an excellent example of the manner in which energy-

resonance between the systems involved can influence the likelihood of energy interchange. The process is, presumably :



the level to which the hydrogen is excited being that equivalent to dissociation. This falls at 4.56 V, while the metastable atom has 4.66 V as compared with the 4.88 V of the higher labile state. This action of the diluent gas in creating, as it were, a reservoir of mercury atoms rich in internal energy but of long life by virtue of their metastability has an interesting effect upon the sensitized fluorescence of metallic vapours, cf. thallium, first studied by Donat [18] and later

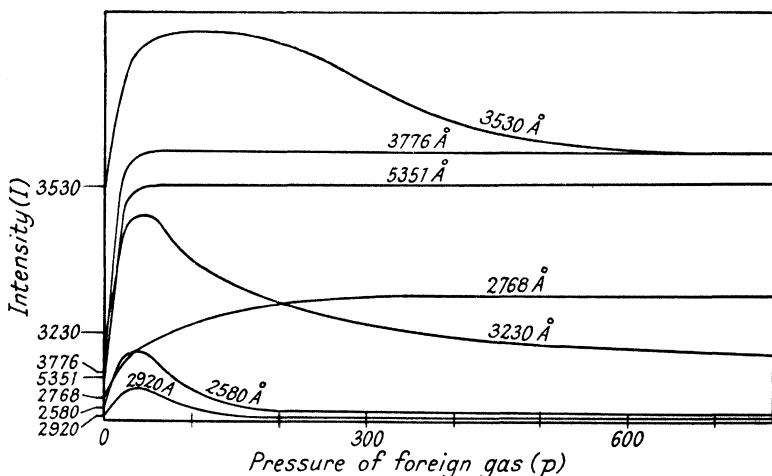


FIG. 16.—Effects of Foreign Gases upon the Sensitized Fluorescence of Thallium (Donat).

repeated under better conditions by Loria [120]. The general type of effect observed is shown in Fig. 16 taken from the paper by Donat [119], although Loria [120] gives reasons for believing that these results may not be quite accurate in their strictly metrical aspects. Hydrogen is very detrimental to the excitation of spectra under such conditions, since it readily reacts with both of the mercury 2^3P states (*supra*). Argon and nitrogen, on the other hand, increase the intensity of the thallium lines to a very marked degree; the green line at $\lambda = 5350 \text{ \AA}$ (from which the name of the element is derived) is brightened some sixteen-fold by the addition of ca. 50 mm. of nitrogen, for example.

With argon, the 2_2S lines at $\lambda = 3776$ and 5350 \AA become more

and more intense as the amount of foreign gas is increased, but above 50 mm. do not further strengthen, whereas those at $\lambda = 3530, 3230, 2920, 2580 \text{ \AA}$, etc., all of which derived from the 3^2S , 3^2D , and 4^2D states, exhibit an initial enhancement followed by a rapid fading-out. This represents the influence of the resonance rule. The lines $\lambda = 3776$ and 5350 \AA are emitted by atoms which upon deactivation in this way would liberate 3.3 and 2.2 V respectively, but the others correspond to intermediate levels and hence a much smaller emission of energy; thus while the Ar at first acts beneficially by increasing the number of excited mercury atoms for excitation of the thallium, this is soon offset by its destructive action upon those states which are, as we have seen, susceptible to collisional termination.

A similar effect has been noticed by Beutler and Josephy [40] in the mercury-sensitized fluorescence of sodium, where the addition of a small amount of nitrogen strongly enhances those lines which are excited by the 2^3P_0 metastable mercury atom. The formation of the metastable state in mercury has been investigated by Klumb and Pringsheim [121] by measurements of the absorption of $\lambda = 4047 \text{ \AA}$, a photocell being employed to record light-intensities instead of the photographic plate more generally used. They find that nitrogen is remarkably effective in inducing the $2^3\text{P}_1 \rightarrow 2^3\text{P}_0$ transition, and consider that this is due, at least in part, to broadening of the line in the primary beam, with increased absorption, through a resonance phenomenon between the bodies concerned. It is of interest to note that the diminution in the intensity of resonance radiation from mercury which accompanies addition of a small amount of nitrogen, does not persist as the partial pressure of diluent is still further raised. At 120 mm., for example, there is considerable fluorescence owing to pressure broadening and enhancement of the absorption of the incident line [389].

A more precise explanation has been given by Pool [122]. Considerable evidence is available that rotational and vibrational states in general show a marked reluctance to change, and in symmetrical molecules the former are metastable. Now in nitrogen, the first and second vibrational levels of the electronic state lie respectively 0.288 and 0.571 V above the $^1\Sigma^0(0)$ state, while above the last of these there are a number of rotational levels of which the 6th is the strongest with 11.2 per cent of the molecules in nitrogen at 20° C ., although the 16th ($^1\Sigma^0(16)$) can account for 2 per cent. If now an atom of mercury be excited optically in the

presence of nitrogen, it has several possible fates, as follows : (Fig. 17)

(a) It may absorb $\lambda = 4358$, be raised to the 2^3S_0 level and return to the 2^3P_2 metastable condition with emission of $\lambda = 5461$. Here it can meet a nitrogen molecule, transfer 0.571 V in a collision of the second kind, and revert to the original 2^3P_1 state, leaving the nitrogen in the second vibrational level ($1^1\Sigma^2(0)$).

(b) It may oscillate between the 2^3P_1 and 2^3P_0 states in similar collisions with the diluent bodies, losing 0.218 V in falling from

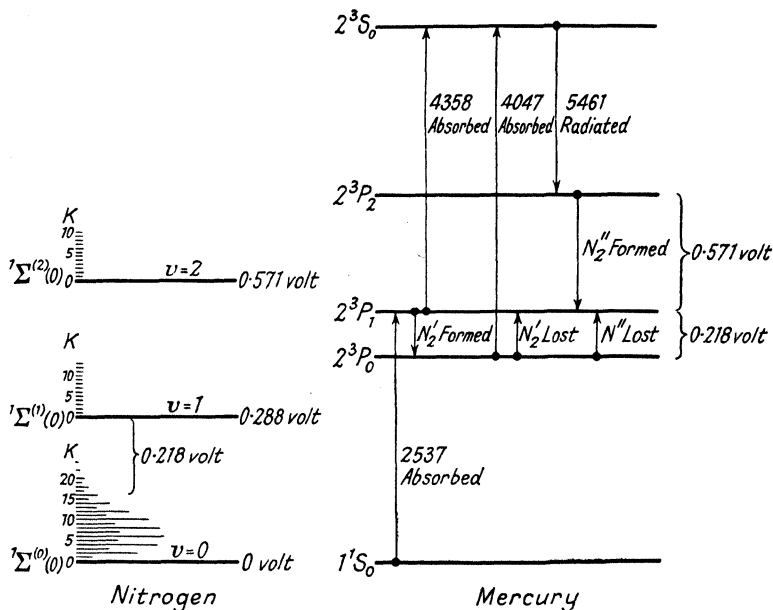


FIG. 17.—Quenching of Mercury Resonance Radiation of Nitrogen (Poole).

2^3P_1 to 2^3P_0 and exciting the nitrogen from $1^1\Sigma^0(16)$ to $1^1\Sigma^1(0)$, or alternatively gaining the same amount of energy on impact with nitrogen in the metastable $1^1\Sigma^1(0)$ state, leaving the donor in the lower $1^1\Sigma^0(16)$ condition. The action of H_2O , CO , CO_2 , NH_3 , and CH_4 is most probably analogous with that of nitrogen since all are rich in vibrational and rotational levels of the zero electronic state and can act as in the case considered here, although their efficacy, quantitatively considered, will naturally vary from gas to gas. Nitric oxide has a very strong effect, but its action has not as yet been satisfactorily accounted for. To effect (a) is due the almost complete absence of transitions originating from the 2^3P_2 level,

although $\lambda = 5461$ is very strong in emission. Moreover, as would be expected from the action of the nitrogen in inhibiting the normal decay of the primarily excited 2^3P_1 atoms, the diminution of the intensity of the resonance radiation is not an accurately exponential function of time, but tends to become slower some 10^{-4} sec. after stimulation, probably due to imprisonment of resonance radiation.

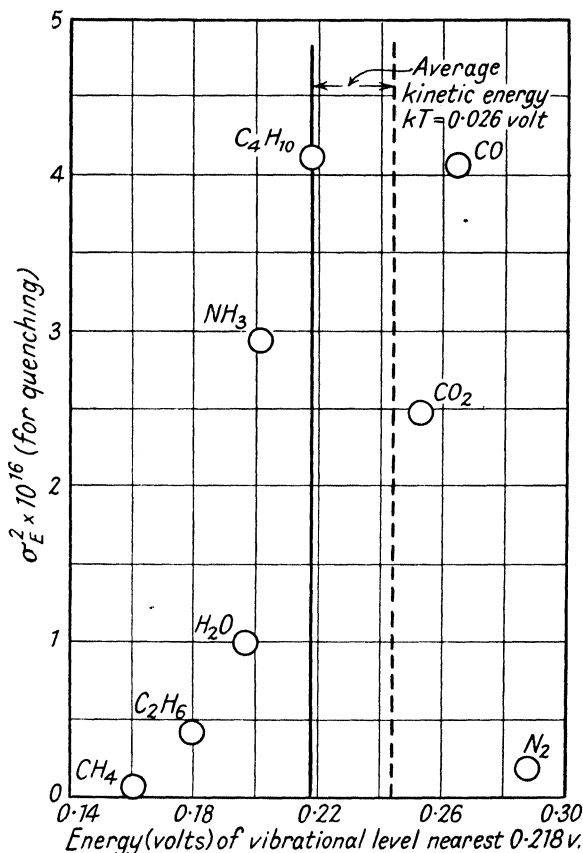


Fig. 18.—“Resonance Curve” for Quenching of Mercury Fluorescence (Zemansky).

Zemansky has suggested [356] that the quenching power of a gas towards mercury resonance radiation is determined by its possession of a strong frequency lying at ca. 0.22 V above the ground state so that by virtue of the excellent resonance it can readily induce the $2^3P_1 \rightarrow 2^3P_0$ transition. This would imply the existence of fairly strong absorption bands in its infra-red absorption spectrum,

whereas nitrogen, which is very effective in this connection, is, in fact, homopolar and transparent in this spectral region. It may well be that here, as in other cases (e.g. the fluorescence of iodine in the presence of foreign gases), selection rules and transition probabilities are modified when collisions are concerned so that a process unlikely when the molecule is left to itself may become much more probable when another body is in the vicinity. (It is, in general, unwise to assume that a particular transition cannot occur merely because optical evidence appears against it, as the recent discovery of the Vegard intercombination band, due to emission from the metastable $A^3\Sigma$ level in nitrogen, shows with considerable emphasis, and due regard must always be had towards the exact circumstances of the case.) Moreover, the existence of a "resonance curve,"

TABLE 8

| Gas. | Cross-section for Quenching. | Energy for Nearest Vibrational Level. (Volts.) | ΔE . |
|--|------------------------------|--|--------------|
| CO | 4.07 | 0.265 | + 0.047 |
| NH ₃ | 2.94 | 0.202 | - 0.016 |
| CO ₂ | 2.48 | 0.253 | + 0.035 |
| H ₂ O | 1.00 | 0.197 | - 0.021 |
| N ₂ | 0.192 | 0.288 | + 0.070 |
| CH ₄ | 0.06 | 0.161 | - 0.057 |
| C ₂ H ₆ | 0.415 | 0.180 | - 0.038 |
| C ₄ H ₁₀ | 4.11 | 0.218 | 0.00 |

which the theory would imply, analogous with those observed by Beutler and Josephy [40] for the sensitized fluorescence of sodium, is well borne out by the evidence given by Zemansky [356] and shown in Fig. 18, and Table 8, taken from his paper. The curve is *not* symmetrical about the line drawn at 0.218 V, where $\Delta E = 0$, but fairly so about $0.218 + 0.026 = 0.244$ V, i.e. of the form to be expected when the mean kinetic energy of 26 millivolts is added to the energy discrepancy of 0.218 V. There is also no marked difference in the quenching effects of those molecules with strong dipole moments (e.g. NH₃) and those which have only weak ones (e.g. N₂). It will, however, be noticed that the point for CO lies far off from the curve, the disagreement being, according to Zemansky, too large to be accounted for by experimental error; it may well be that here, as in Manley and Duffendack's experiments upon the excitation of magnesium spark lines by ionized neon (pp. 16-17), the

type of level concerned is of nearly as much importance as the energy discrepancy.

(For details as to the units wherein the cross-sections for quenching are expressed, the reader is referred to Zemansky's paper [356].) An even better resonance curve has been obtained by Evans [114] from measurements of the quenching effects of D_2O , D_2 , and ND_3 as compared with H_2O , H_2 , NH_3 .

Zemansky's suggestion, it will be noticed, is only a more formalized modification of the earlier views of Mitchell [132] and others mentioned on p. 91.

Apart from these studies with mercury, the effects of foreign gases upon resonance radiation do not seem to have been much investigated except in the case of iodine, where our knowledge of the subject is almost entirely due to Wood and his collaborators; a summary of the work is given in Chapter 19 (pp. 623-6) of the third edition of his "Physical Optics" (see also [146]). When iodine vapour is irradiated at room temperature by the very narrow line at $\lambda = 5461 \text{ \AA}$ given by a Cooper-Hewitt mercury lamp operated at a low voltage, it emits a fluorescence spectrum consisting of a series of doublets rising up to the 27th order, with an almost constant frequency difference as between one group and the next, and extending from the green to some distance in the infra-red. Since the excitatory line is so narrow as to cover only one of the iodine absorption lines, it follows that the molecules which are excited must all be raised from a common level, and fall to the same electronic state upon fluorescence, although by reason of the anharmonic nature of the vibrations transitions to all possible vibrational states of this lower level are to be expected. Moreover, since it is known from an analysis of the spectrum that the change in electronic levels here involved may permit of a change of 44 in the vibrational quantum numbers of the initial and photoexcited states, the range and complexity of the fluorescence spectrum may well be understood. The doublet nature of the spectrum arises from the selection rule, whereby the rotational quantum number, j , is permitted to change either not at all or by ± 1 ; in the former case, the Fortrat diagram would show a Q branch, and in the latter, as in the example under consideration, only P and R branches. If, then, every change in the vibrational quantum n is accompanied by a corresponding change of ± 1 in j , a transition from the upper vibrational level to a lower one will give two lines, according as $j'' - j'$ is $+1$ or -1 . Addition of a small amount of a noble gas,

in such an experiment, develops a band spectrum at the expense of the doublets, although the total amount of the fluorescent light does not alter much [305]. This is attributed to alterations of both n and j when photoexcited iodine molecules undergo collisions with the diluent bodies, whence the fluorescence is emitted not by molecules in a common upper state, but in very many, so that a band series becomes superposed upon the original doublets. In this case, the only lines observed in states with *even* values of j , the highest level of the photoexcited state having $j' = 34$, and hence it is to be concluded that where the electronic quantum number remains unchanged on collision, the rotational quantum number alters only by an even number. The reasons for this involve considerations upon symmetrical and unsymmetrical states in the iodine molecule, and is too complicated to be discussed here; a full account, with a bibliography, is given by Jevons [124]. It will be noticed that the selection rule here breaks down, since j is altering not by ± 1 but by 2 [see also 262, 263, 296].

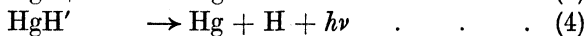
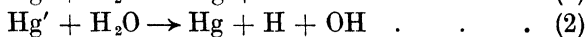
Nitrogen dioxide also fluoresces faintly under the influence of the mercury lines at 4358 and 4047 Å, and the intensity is markedly dependent upon the overall pressure, diminishing by one-half between 0.001 and 0.02 mm. This cannot be attributed to alterations in the absorption of the light through any pressure-broadening effects and it would appear most probable that the nitrogen dioxide itself is an extremely efficient quenching agent, while, upon the assumption that the life of the photoexcited molecule is of the usual order (ca. 10^{-7} sec.) the destruction of the fluorescence as a function of pressure indicates an effective cross-section of some ten times that given by viscosity data. As in Stuart's investigations with mercury [108], diluent gases act in quite a specific manner, the relative quenching powers, referred to nitrogen dioxide as unity, being 0.87, 0.29, 0.24, and 0.15 for carbon dioxide, nitrogen, oxygen, and hydrogen respectively [272, and references there cited].

The second type of quenching, i.e. that which results from chemical action accompanied by a change in the composition of the system, is well illustrated when hydrogen is the gas concerned.

If a mixture of hydrogen and mercury vapour be irradiated by the mercury resonance line at $\lambda = 2537$ Å, the hydrogen undergoes dissociation and exhibits many of the characteristics of the "active" hydrogen obtained by means of the electric discharge; for example, it can reduce copper oxide, combine with oxygen to give water and small amounts of hydrogen peroxide [125, 126], and possesses the

enhanced thermal conductivity to be expected of a mixture of atoms and molecules [127, 128]. Since the heat of dissociation of hydrogen (4.56 V) lies so closely to the energy of the 2^3P_1 and 2^3P_0 states of mercury, both of which are, as we have already seen, copiously formed under these conditions, it would be anticipated that the production of the atoms is a simple reaction in which the whole of the energy of the donor or donors passes into the vibrational levels of the molecules and hence leads to disruption.* It is certain that hydrogen *can* be broken up, since Calvert has recently found that hydrogen mixed with xenon and exposed to the xenon resonance line at $\lambda = 1469 \text{ \AA}$, vessels with fluorite windows being of necessity employed, shows both an increase in pressure and an ability to reduce tungsten trioxide [129].

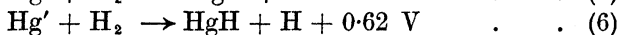
In the parallel experiment with optically excited mercury, however, the reactions are somewhat complex, but of much the same type when both hydrogen and water vapour are under examination. Gaviola and Wood have found [130] that in both cases bands due to HgH appear in the fluorescence, but whereas with the latter gas they exhibit low rotational characteristics with the maximum intensity in the heads of the bands, in the former case the intensity is more marked in the "tails" and the rotational aspects are strong. These differences were attributed to the loss of energy from the excited mercury hydride only upon collision with water vapour, and not with other gases such as hydrogen or nitrogen, the overall reaction scheme being taken as :



Since only excited states were here envisaged, there should be a dependency between the rotational properties of the bands and the pressure of the diluent gas, while the 0.37 V dissociation energy of the hydride would argue considerable stability at room temperature, neither of which effects were actually observed by Beutler and Rabinowitsch [131], who have made a further study of the problem and reach conclusions different from those advanced by Gaviola and Wood. From measurements upon the quenching of the resonance radiation and the absorption lines deriving from the

* It does not seem likely that 2^3P_0 atoms are here formed in quantity, since the line $\lambda = 4047 \text{ \AA}$ is absent in absorption.

metastable 2^3P_0 state, they concluded that the formation of the hydride occurs through reaction with the *metastable* atom and not the higher labile state, according to the processes :



The efficiencies of the two reactions were found to be some 10^{-4} to 10^{-3} in the case of water vapour, and ca. 8 for hydrogen, the ordinary gas-kinetic equations being employed in the calculations of the number of collisions occurring; the doubtful validity of this in reactions involving excited states has already been pointed out, and may account for the apparent 800 per cent probability of reaction 6. They were also able to show that the HgH derived from water has a rotational quantum number of only 4, whereas that from hydrogen has ca. 20, the differences in the rotational characteristics persisting in spite of many collisions with the nitrogen which was added to give a large concentration of metastable atoms. This stability of the rotational properties of the hydride is recognizable through the nature of the bands emitted as a result of the secondary excitation of HgH by Hg', when the radiation is specific according to the particular modification of mercury hydride from which it derives.

If foreign gases are added to assist in the transition of the 2^3P_1 state to the lower 2^3P_0 level, the ratio of the concentrations of the two species becomes some 1 : 2000, and the ultimate deactivation of the metastable atom is not controlled by ordinary gaseous diffusion to the walls, but by an energy diffusion process involving collisions of the second kind with other bodies present, as in the parallel case of the very slow escape of resonance radiation from such a system. This, and other papers by Beutler and his collaborators may be very highly recommended both for their admirable bibliographies and the thoroughness with which the problems are attacked. Oxygen can apparently induce both "physical" and "chemical" quenching. As regards the former, Mitchell has suggested [132] that it may be due to the existence of a vibrational level of the ground electronic state at, or very close to, 4.88 V, so that there will be almost perfect energy-resonance between the systems. Using data obtained by Ossenbruggen [133] upon the Schumann-Runge bands, he calculates—making the assumption that the levels converge regularly—that the state $n = 35$ will have an energy of 4.86 V. This involves a somewhat extended extrapolation, since those states actually observed go only to $n = 17$,

and it is now known that the value of D for oxygen obtained in this manner (6.65 V) is too high. Hence, although the exact location of the required energy level does not seem permissible, we may nevertheless conclude that a state does exist on the oxygen molecule wherein good resonance with the 2^3P_1 mercury atoms may obtain, to produce the large quenching efficiency observed.

The concept is also useful as providing a reaction mechanism for the production of ozone, which is observed in this case [134]. Its genesis as a purely photochemical effect may be traced with a light of wavelength greater than that required to dissociate any oxygen molecule, so that the simple union of O and O_2 to give O_3 is not possible [135]. The same objection holds for the sensitized reaction, since the heat of dissociation of oxygen (5.1 V) is greater than the energy (4.88 V) of even the labile 2^3P_1 state in mercury, and the discrepancy of 0.22 V is too large to be made up from the kinetic energies of the reactants since at room temperatures this last is only 0.026 V per gm. mol. Some kind of cumulative excitation process would therefore seem essential, probably involving one of the low vibrational states of O_2 such as the $1^1\Sigma$, which has been found by Childs and Mecke to persist as long as 7 seconds under appropriate conditions [285]. The reaction would then be of the type: $O_2' + O_2'' \rightarrow O_3 + O + \text{K.E.}$, the superscripts denoting molecules in different states of excitation. Since, however, a certain amount of mercuric oxide may also be detected in this reaction,* the further processes: $Hg' + O_2 \rightarrow HgO + O$, or $Hg + O_2' \rightarrow HgO + O$, followed by $O + O_2 \rightarrow O_3$, cannot be eliminated, but the balance of evidence indicates that they are not of so much importance as those already discussed.

Other examples of specific chemical effects in collisions of the second kind are discussed in Chapter VI.

* The formation of mercuric oxide under these circumstances has recently been turned to good account for separation of the isotopes of the metal [358]. Mercury vapour was exposed, in the presence of a small amount of oxygen, to the hyperfine components of $\lambda = 2537 \text{ \AA}$, obtained by filtration of the resonance line through a column of mercury vapour placed in a strong magnetic field [357], so that only the isotopes Hg200 and Hg202 should have been excited. Examination of the deposit thus obtained after only a short experiment showed that the normal ratio $Hg(200, 202)/Hg(198, 199, 201, 204)$ may be enhanced as much as fourfold, especially if a little nitrogen be also present along with the oxygen. This last observation would suggest that the reaction is more complex than was at first supposed, and it seems to merit further study.

CHAPTER VI

CHEMICAL REACTIONS INVOLVING COLLISIONS OF THE SECOND KIND

The principles discussed in the earlier chapters lead naturally to the assumption, which is fully in accord with experience, that an atom endowed with an ability either to emit or absorb energy rather more easily than others in its vicinity, will be bound to affect both the degree and nature of the chemical reactions which may be taking place in the system. For example, a photochemical reaction of hydrogen and oxygen is undetectable, even with the shortest wavelengths, when the pure gases are used, but proceeds with ease in the presence of a trace of mercury under the influence of $\lambda = 2537$ [364, 368] and at $\lambda = 4300$ with a similarly small amount of chlorine [365]. The decomposition of oxalic acid in aqueous solution has a quantum yield γ of 0.0041 with $\lambda = 3000$ [366], but in the presence of a small amount of a uranium salt $\gamma = 1$ at practically the same wavelength [367, 369]. Here then, as in many other cases, the addition of a small amount of another substance is markedly affecting both the ease of the reaction and the yield of products per unit of energy supplied, and so to a certain extent these "sensitizing agents" may be regarded as photochemical catalysts. The analogy cannot, however, be carried too far, since whereas the catalyst proper merely influences the velocity of a reaction without affecting the final equilibrium, sensitized photoreactions frequently take place under conditions where, in the absence of the sensitizer, no detectable changes can be found even after the most prolonged experiments; the interaction of hydrogen and oxygen in the presence of mercury [364, 368] may be quoted as an example. Conversely, a catalytic reaction may in some cases approximate very closely to a collision of the second kind with good resonance between the systems, plus a modified Auger effect, so that the process becomes one of electron interchange; the Haber synthesis of ammonia, and the conversion of NH_3 to HNO_3 by oxygen in the presence of platinum illustrate this type of parallelism. The difficulty of making too much of this analogy is, however, seen at once

from other reactions such as the Deacon process for chlorine, and the combustion of carbon, where intermediate compounds of considerable stability are found and may easily be isolated, so that the changes no longer involve the excited and metastable states with which we have so far been mainly concerned. Hence if comparisons are to be instituted, every reaction must be judged upon its own characteristics.

Sensitized reactions fall, in general, into two main classes. In the first, the sensitizer absorbs energy from an external source, and in a collision of the second kind conveys the whole or a part to one of the other molecules present, thereby transforming it into a reactive condition; this, in a photochemical reaction, implies ability of the sensitizer to absorb light in a spectral region where the other substances are transparent or at any rate not capable of more than very feeble excitation to the levels requisite for reaction. In the second, the sensitizer influences the course of the reaction through absorption of energy from excited bodies formed in the process, thereby breaking reaction chains. Recent studies such as those made by Johnson [198, 201] suggest that sensitizers whose influence has hitherto been regarded as confined to the gas phase, may also have a profound influence on surface conditions as well, introducing a third factor compounded of both the considerations advanced above, but the evidence here is so far too slender to justify its further attention [cf. pp. 67, 78, 79].

In the present chapter we shall discuss a number of reactions which exemplify the influence of collisions of the second kind in processes of a chemical nature. Such a study cannot be complete in any work of the scope of this monograph, and all that will be attempted is the provision of a number of indications to act as guides both for those interested in the theoretical aspects of the principle with which we are concerned, and for others who have encountered, in the course of experimental researches, puzzling phenomena which may be explicable by the generalizations expounded in this book.

The Sensitized Interaction of Hydrogen and Carbon Monoxide.

The combination of hydrogen and carbon monoxide, in the presence of mercury, when illuminated by the full light from a mercury vapour lamp, has recently been the subject of an admirable research by Frankenburger [370]. The reaction products, which vary both as regards total yields and relative concentrations, with

the experimental arrangements, are formaldehyde and glyoxal, and under the best conditions from 1 to 1.5 (CHO) groups are formed for every quantum of $\lambda = 2537 \text{ \AA}$ absorbed. High flow speeds, low temperatures, and an equimolecular mixture of the gases are essential to the most favourable yields. The reaction appears divisible into four well-defined stages, as follows :

1. A mercury atom absorbs $\lambda = 2537$ and is raised to the 2^3P_1 state, falling thence to the lower 2^3P_0 level in a collision of the second kind with a molecule of carbon monoxide. Some of these metastable molecules may be lost through absorption of $\lambda = 4046 \text{ \AA}$ (the light being unfiltered) so that formation of the 2^3S_1 state renders them ineffective towards hydrogen. The majority, however, survive for the reaction.

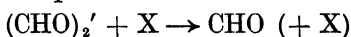
2. Hydrogen molecules are dissociated :



Some recombine on the walls, with the formation of local high temperatures, but by adequate cooling the surfaces are kept sufficiently poisoned to reduce this reaction, and if it occurs, to minimize its possible inimical effects upon the other stages.

3. The bulk of the H, however, reacts with CO in the presence of a third body to give the radical (CHO), a certain amount of the product being lost (i) by reason of the reversible nature of the reaction ($H + CO + X \rightleftharpoons HCO + X + 4000 \text{ cal.}$ and (ii) through photochemical destruction, both of these latter processes being again easily suppressed by proper choice of experimental conditions.

4. Two radicals combine to form a nascent glyoxal molecule $(CHO)_2'$, which then passes either to stable glyoxal, or to formaldehyde with the separation of CO :



X being the requisite third body since the reactions are respectively 127 and 78 cal. exothermic. In the first case, $\gamma = 2$, and in the second, unity, whence it follows that if the reaction scheme is correct, the observation that the molecular ratio of formaldehyde to glyoxal in the product ranges from 60 : 40 to 80 : 20, will necessitate that γ for the *overall* reaction shall lie between $\frac{60 + (2 \times 40)}{100}$

and $\frac{80 + (2 \times 20)}{100}$, i.e. between 1.4 and 1.2; the values actually

found being 1 — 1.5, there is clearly strong evidence as to the correctness of Frankenburger's ingenious theory.

The Synthesis and Decomposition of Ozone.

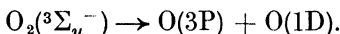
I. The formation of ozone by illumination of oxygen with ultra-violet light was one of the first photochemical processes to be studied, it having been observed by Lenard as long ago as 1900 [400]. This discovery was soon followed by another, viz., that ozone can be photochemically decomposed, and that the 2 per cent generally obtained as the optimum yield using a source such as the condensed aluminium spark really represents an equilibrium which can be approached from both sides [401]. [For summaries of the older literature see 420.]

A discussion of the mechanisms involved must be preceded by reference to the absorption spectra of both oxygen and ozone. The principal band series of oxygen are as follows:

(a) The Schumann-Runge series

$$({}^3\Sigma_g^- \rightarrow {}^3\Sigma_u^-; \lambda\lambda = 1925-1757 \text{ \AA}),$$

whose convergence limit lies at $\lambda = 1751 \text{ \AA}$ and is followed by a continuum reaching at least to $\lambda = 1300 \text{ \AA}$. An oxygen molecule dissociating from the upper states of these bands passes into one 2P and one 1D atom [402]:



(b) The Herzberg series (${}^3\Sigma_g^- \rightarrow {}^3\Sigma_u^+$; $\lambda\lambda$ 2600–2430 \AA) converging at $\lambda = 2429 \text{ \AA}$, corresponding to dissociation into two normal atoms [402]. This may be related to another series obtained in high pressure (500 Ats.) or liquid oxygen between $\lambda\lambda$ 3813–2490 \AA and supposed—since both their intensity [403] and the extinction coefficient in the continuum which succeeds them [404] vary as the square of the pressure—to be due to an O_4 molecule [405]. [For a discussion upon O_4 , see 421.]

(c) The Badger-Mecke series ($\lambda\lambda = 7800-5780 \text{ \AA}$) which has for some time been known in celestial spectra but only recently obtained [406] in the laboratory by the use of very long absorption tubes. It is very feeble, since it corresponds to the ${}^3\Sigma \rightarrow {}^1\Sigma$ transition whereby the metastable molecule with an energy of 1.62 V is formed [285].

It will be clear, in view of the foregoing considerations upon the absorption spectra of oxygen, that the formation of ozone by irradiation of oxygen with $\lambda = 2070 \text{ \AA}$ and $\lambda = 2530 \text{ \AA}$ must necessitate

two mechanisms of reaction. This was realized by Warburg [404, 410] who studied the synthesis in streaming oxygen at pressures up to 300 Ats. under the influence of the above-mentioned lines. With $\lambda = 2070 \text{ \AA}$ and pressures not exceeding 125 Ats., $\gamma = 3$, which Warburg explains by the mechanism :



it being assumed that step (3) is of infrequent occurrence relatively to (2) so that three oxygen molecules are removed for each quantum absorbed. Above 125 Ats., however, γ diminishes, which Warburg interprets by postulation of another type of absorption above this limit, so that excitation of the oxygen to the level for dissociation is prevented owing to removal of energy by other molecules in the vicinity. Since this pressure region is that wherein Holtsmark-Lorentz broadening becomes important, the suggestion would appear entirely reasonable (cf. pp. 71, 72).

With $\lambda = 2530 \text{ \AA}$, which cannot induce dissociation, another sequence involving excited molecules must be adopted, and Warburg suggests :



or

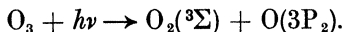


Since the reaction here necessitates the absorption of 68.2 Cals. whereas $h\nu \equiv \lambda = 2530 \text{ \AA}$ can furnish 112.2 Cals. the reaction is energetically possible while the abundance of termolecular collisions at such high pressures could easily provide for the dissipation of the excess energy and hence account for the observed quantum yield of three. It may be mentioned that the value of γ is susceptible to pressure as with $\lambda = 2070 \text{ \AA}$, and for the same reasons. A suggestion by Wulf [405, 411] that the reaction proceeds through dissociation of O_4 by $\lambda \leq 2400 \text{ \AA}$: $\text{O}_4 \rightarrow \text{O}_3 + \text{O}$, and that the O_4 is excited by $\lambda \geq 2530 \text{ \AA}$ to give a sequence of events much as in reactions (4) —(6) (*supra*), does not now seem tenable since it has more recently been found that $\gamma = 3$ in oxygen at atmospheric pressure (where the concentration of O_4 would be negligible) under the influence of light in the range $\lambda\lambda$ 1700–1900 \AA [412].

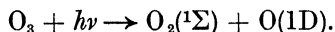
II. Ozone has two main absorption series :

(a) The bands in the range $\lambda\lambda$ 4000–10,000 \AA , which have a

structure indicating predissociation and at the convergence limit give rise to a reaction :



(b) The intense ultra-violet bands ($\lambda\lambda$ 2700–3300), which converge to a continuum (probably extending back into the region of band absorption) below the first of the above limits [407–409]. The process here is not very well established, because of the difficulty in locating the exact position of the convergence limit, but it most probably corresponds to :



(From the heat of formation of ozone ($3\text{O}_2 \rightarrow 2\text{O}_3 - 68.2$ Cals.) and the energies of the $^1\Sigma$ and 1D states (37 Cals. and 45.2 Cals. respectively) $h\nu$ may be calculated as equivalent to $\lambda = 2650$ Å, in good agreement with the usually accepted experimental value $\lambda = 2700$.)

The decomposition of ozone may be brought about either (i) by ultra-violet or (ii) by red light. The first process has long been known (*supra*), but the latter was discovered by Griffith [415, 416] as recently as 1921. The two reactions will at first be treated separately.

Decomposition of Ozone by Ultra-violet Light. The majority of present-day conclusions upon this reaction originate in the classical investigations made by Warburg [404]. Using $\lambda = 2530$ Å, he found that γ for dry ozonized oxygen at a total pressure of one atmosphere is strongly dependent, after an initial stage, upon the concentration of ozone in the mixture (Table 9).

TABLE 9
VARIATION OF γ WITH CONCENTRATION OF OZONE

| % O ₃ | γ | % O ₃ | γ |
|------------------|----------|------------------|----------|
| 0.18 | 0.31 | 0.75 | 0.50 |
| 0.35 | 0.28 | 1.85 | 0.76 |
| 0.47 | 0.29 | 2.92 | 1.66 |
| | | 9.29 | 3.52 |

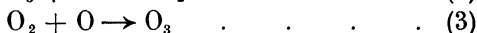
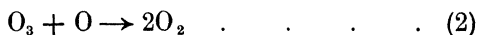
This observation is parallel with another made much earlier by Frl. von Bahr [424], viz. that the quantum yield increases very rapidly as the total pressure of a dilute mixture is decreased (*vide supra*).

When higher concentrations are used in the presence of water vapour (17 mm.), γ also rises with the amount of the reactant present, values nearly twice as great being obtained as in the parallel experiments with dry ozone of equivalent concentrations, but decreases as the intensity of illumination is made greater, the results being approximately described by: $\gamma = K \cdot \sqrt{\frac{[\text{O}_3]}{I}}$, where K is a constant depending on the wavelength of the light, $[\text{O}_3]$ is the concentration of ozone, and I the intensity of the line concerned.

Foreign gases exert a marked accelerating effect upon the velocity of reaction and hence lead to an increase in γ ; in highly ozonized oxygen, γ is generally ca. 0.3, whereas addition of excess of nitrogen brings it up to 1.07, and excess of helium to 1.7 [404]. Further researches by Griffith and his school [415, 416, 419] and by Kistiakowsky [385] have shown that the enhancement increases in the order: $\text{O}_2 \rightarrow \text{N}_2 \rightarrow \text{CO}_2 \rightarrow \text{He}$. Hydrogen has also a strong effect, but interpretation is here more difficult since chemical action (formation of water) is considerable [425]. As reaction mechanism, Warburg suggested a primary dissociation of the ozone:



followed by:



Since γ for the first stage is unity, the quantum efficiency for the overall reaction will be 2 at its maximum but be reduced to an extent depending upon the likelihood of stages (3) and (4), which offer to the oxygen atom alternative methods of elimination not involving the destruction of ozone. Stage (3), of course, regenerates ozone, but since the amounts of free oxygen present would be very small—as the O_2 is formed by the decomposition of the O_3 —it follows that the most probable value for γ in the presence of the diluents—which were proved not to undergo any chemical change—should lie between 1 and 2 and be much less—because of the greater likelihood of stage (3)—in ozonized oxygen.

The pressure effect noted by Frl. von Bahr [424] naturally follows from stage (3), which will become increasingly less probable as the pressure decreases, the more especially since it will probably necessitate the presence of a third body ($\text{O}_2 + \text{O} \rightarrow \text{O}_3 + 24.7 \text{ Cals.}$). The very high values found for γ when the concentration of ozone

is high, or when foreign gases are present, is accounted for by stage (2). Since it is 92.8 Cals. exothermic a foreign gas capable of acting as acceptor for the energy liberated will exert a strong positive catalytic effect, but not raise γ above 2 (*supra*). (The differences in the accelerations induced by nitrogen and helium need not surprise us in view of all that has been said on previous pages as to the highly specific effect of the various gases in influencing such collision-processes by abstraction of energy from the primary reacting systems.)

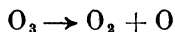
Other ozone molecules in the vicinity may, however, be wholly or partially activated, in the same manner, to the point at which they readily decompose, a chain reaction thus being initiated; this will account for the optimum value of 8 found for γ with 8 per cent O_3 at $\lambda = 2090 \text{ \AA}$. In support of this hypothesis, Warburg points out that K (*supra*) is at its minimum when $\lambda = 2530 \text{ \AA}$ is used, i.e. when absorption of light by the system is at its maximum,* suggesting that the larger the volume of the reacting gas over which the absorption is distributed, the more effective is the radiation thus introduced, i.e. that each potentially reactive centre desires the untrammelled co-operation of a number of other molecules, hitherto unaffected, for the maximum utilization of its energy.

Decomposition of Ozone by Red Light. Early researches upon this reaction [385, 415, 416, 419] showed that γ is invariably much less, even under the best conditions (low overall pressure and high concentration of ozone) than in the parallel decomposition by ultra-violet light. Total pressure, and addition of foreign gases, affect the quantum efficiency as before, the latter in exactly the same order. (Referred to O_2 as unity, the inhibiting effects are: He 0.13, N_2 0.3, and CO_2 0.8 [385].)

Similar observations that there is a marked "inert gas effect" in the thermal decomposition of ozone [417, 418, 427] and in its photochemical reaction with hydrogen led for some time to the supposition that both the optical and thermal processes necessitate the primary formation of an excited molecule, whose tendency either to dissociate *per se*, or to enter into association with another unexcited ozone molecule to form a complex which then suffers destruction, is influenced by the naturally variable "quenching" powers of the different foreign gases concerned. Added weight to this opinion was furnished by the then accepted value (163

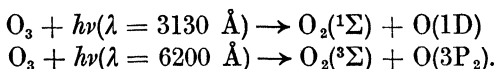
* For data upon the extinction coefficient of ozone in the ultra-violet see [413, 414], and references there cited.

Cals. $\equiv 7.1$ V) for the heat of dissociation of oxygen which rendered impossible, on a simple basis of energetics, a dissociation of O_3 to $O_2 + O$ under the action of red light. This last process may now, however, be admitted, since with D for oxygen as 117.3 Cals. $\equiv 5.1$ V, the reaction :



is only 24.7 Cals. endothermic (*supra*) whereas $\lambda = 6200$ can furnish ca. 45 Cals. (A discussion is given by Griffith and McKeown [420].)

An extensive study recently made by Schumacher [422, 423] has shown that under equivalent conditions of experiment as regards concentration of ozone, presence of diluents, overall pressure, etc., γ is the same for $\lambda = 3130 \text{ \AA}$ as for $\lambda = 6200 \text{ \AA}$. This very important result indicates, according to Schumacher, not merely the same type of reaction with equal velocities in both cases, but identical activity of both unexcited and excited oxygen atoms, for which there is already other evidence. It may be recalled that the processes are:



These conclusions appear to conflict with the data of Warburg, who found γ to be as high as 8 under appropriate conditions, and we may reasonably entertain a certain doubt as to there being no difference in the reactivities of $O(^1D)$ and $O(^3P_2)$. On the other hand, it is always possible that since Warburg used $\lambda = 2530 \text{ \AA}$ as his ultra-violet line, as compared with $\lambda = 3130 \text{ \AA}$ adopted by Schumacher the oxygen atom (1D) set free in the primary reaction could, by virtue of its higher kinetic energy, give rise to an $(O_2 \cdot O_2')$ complex rather more effective in promoting chain formation than that originating from the atom liberated by light of the larger wavelength.

The Sensitized Photographic Plate.

It seems by no means improbable that collisions of the second kind may in part be responsible for the ability of certain substances to sensitize a photographic plate towards the light of long wavelength, where its response is usually negligible. A preliminary discussion of some points of photographic theory is, however, necessary. [Summaries of this subject are given in 430, 431.]

A number of very important facts have to be recognized, as follows :

(a) A given preparation of silver halides will often exhibit the

widest variation of response towards light according to the nature of the gelatin wherein it is incorporated. This is now known to be associated with the formation of minute traces of silver sulphide from thiocarbamides, derived from allyl isothiocyanate present in the gelatin [428, 429].

(b) The effective action of the light, as regards photographic action, is restricted to minute nuclei upon the surface of the silver halide crystals, consisting certainly of Ag_2S , and in some cases of metallic silver as well [432, 428, 429, 431]. This cannot mean either that the radiation exhibits a kind of structure *vis-à-vis* the crystal, or that it is selectively absorbed at these foci, which can be reproduced by purely chemical means such as treatment with hydrogen peroxide or sodium arsenite [433, 434] in the absence of light. Rather would it suggest, according to some authorities, that the whole of the radiant energy absorbed by the crystal is transmitted through the lattice to a weak point round the nucleus, the grain thus acquiring developability through liberation of silver [435]. (Unexposed grains will, in fact, develop if treated with finely divided silver [439].) If, on the other hand, we regard these nuclei, which are distributed mainly along the edges and corners of the crystals [436] as representing zones where the light has induced some break-up of the normal lattice owing to local weaknesses, we can then account for (a) the quantum yield (i.e. $\text{Ag}/h\nu$) being low* and (b) the number of such centres which appear in unit time being proportional to the number of quanta absorbed by the crystal [437]. The well-established fact that the larger grains are more sensitive to light than the smaller ones [440, 441] is also explained by this theory of local strains, since it is a matter of common experience that large crystals invariably possess many more imperfections of structure than do the smaller ones, owing to stresses set up in the process of formation.

The sensitization phenomena wherein we are here interested arise out of the classical observation made by Vogel in 1873, i.e. that photographic plates normally insensitive to wavelengths greater than $\lambda\lambda$ 5000–6000 Å can be made to respond to this part of the spectrum by treatment with dyes such as eosin. Vogel realized that actual adsorption of dye by the silver bromide is essential, and that the dye shall possess a strong absorption band in the spectral region to which the plate is to be sensitized, but that even then the effect

* The evidence here is conflicting, but it appears that only under special conditions does γ approach unity [see 438].

is confined only to a small proportion of those substances which fulfil both criteria. (An account of this pioneer work is given by Luppö-Cramer [431] and Eder [442].)

In recent years, much attention has been devoted to sensitization by cyanine dyes, which consist essentially of heterocyclic rings joined by a conjugate chain ; a typical example is pinacyanol, whose structure was first established by Mills and Hamer [445], and by their use the response of even fine-grained emulsions has been extended as far as $\lambda = 14,000 \text{ \AA}$. (Such plates may be employed to take perfect photographs in complete darkness, and Dr. C. E. K. Mees recently exhibited, at a Friday Evening Discourse in the Royal Institution, several admirable portraits obtained with electric flat-irons as the illuminants [cf. 443].)

We may now discuss the *modus operandi* of these sensitizing agents. In the first place, it is clear that the effect cannot be attributed to a simple process of fluorescence, whereby the sensitizer absorbs "inactive" radiation and re-emits it in a form to which the plate is susceptible. Although anti-Stokes terms may often be formed in the spectrum of a fluorescent body, their intensity is so small as to render quite negligible any effects due to the emission of light of wavelength shorter than that of the excitatory radiation. Moreover, were this the case, there would seem no valid reason for the dye to be adsorbed upon the silver bromide crystals and a much less intimate union should be equally effective.

It would seem much more likely that we have to deal with a primary absorption of light by the dye, followed by a modified Auger-type of energy transfer to the silver bromide crystal, whose lattice will be to a certain extent distorted by the binding forces developed during adsorption, especially if this be of the very intense "activated" modification [cf. 444]. Under such conditions, the stresses in the crystals would be much enhanced, and fission of the lattice favoured although the quantum yield of the radiation might be relatively small. It might thus be expected that differences in the sensitivity of the various faces of the crystals would develop—especially if the anisotropic hexagonal silver iodide were present—since the adsorptive properties, along with the physico-chemical characteristics such as solubility, etc., change from face to face [cf. 446]. Experimental evidence upon this point is so far lacking.

The changes must clearly be associated mainly with the silver salt, since were the dyestuff molecule appreciably distorted its absorption in the adsorbed state would differ somewhat from that

ordinarily observed, i.e. the sensitization would not occur in the same spectral region as that occupied by the absorption bands of the sensitizer, and there is as yet no evidence that is the case. (We may also conclude, from this fact, that the dye is not bound to the crystal at the chromophoric group, or at any rate by forces which can seriously affect this part of the molecule.)

Mitogenetic Radiation.

The phenomenon of cumulative excitation, to which allusion has already been made (pp. 22, 23), has in recent years received much attention in the field of chemical kinetics because of its bearing upon the question of reaction velocities and energies of activation, in unimolecular reactions in particular. It is now recognized that a complex molecule may absorb small amounts of energy over a series of collisions, until its total potential energy, distributed over several degrees of freedom, is vastly in excess of its normal dissociation value. The iodine molecule, for example, may hold up to seven times the amount required to split it up to atoms. Such a body thus behaves very much like a metastable molecule, indifferent in large part to collisions, until some process of an internal character leads to a sudden switch of all the energy on to one or two degrees of freedom, with the result that violent action follows. It would seem that such a process underlies the phenomenon of mitogenetic radiation, if indeed this is an objective reality and not merely the result of researches conducted without adequate controls in the most difficult of all fields, i.e. experimental biology.

In 1923 Gurwitsch claimed that if an onion root be placed vertically so that its meristematic area is perpendicular to another root placed in a horizontal position and not more than 4 cm. away, then the rate of division of the cells in the first root will be very greatly enhanced, increases of the order of 80 per cent sometimes being observed. The effect is not influenced by water and other substances which do not interfere with normal cell division, but interposition of a sheet of glass between the units being examined stops the stimulative action. Later work suggested that the mitogenetic influence between the roots is propagated rectilinearly, can be reflected by mirrors and focussed by lenses, and cut off by media not transparent above the near ultra-violet, whence it has been assumed that we have to deal with a radiation of wavelength of the order 2000–3000 Å. Since the quantum here is so large, we must assume that a process of cumulative excitation is operative, the energy changes in biological reactions being generally of a low order

and rarely exceeding 20 Cals., equivalent to emission in the infra-red.

Gurwitsch considers that this M-radiation may originate in a chemical reaction such as an exceptionally vigorous oxidation of glycogen to lactic acid and further products, or in an enzyme process similar to the oxidation of the glucoside luciferin by luciferase, this latter reaction being chemiluminescent with emission in the visible spectrum. He claims to have separated from onion roots two preparations which are mitogenetically inactive alone, but active when mixed, giving off strong radiations for as much as an hour in this case.

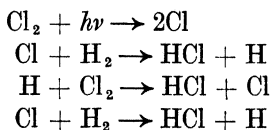
The phenomenon has received extensive study and with a wide diversity of creatures ranging from tadpoles' heads to the bacteria and sea-urchins' eggs, but from the tumult of a vigorous controversy—much of it conducted with the true *odium theologicum*—the fact does emerge that nobody has so far recorded emission of this radiation using non-living matter as the receiver; devices such as Geiger counters, and plates hypersensitized to the near ultra-violet region of the spectrum, have failed to show any effect even after experiments of eighty-nine days' duration.

Moreover, a considerable number of the initial premises of Gurwitsch and his school, such that there is normally a radial symmetry of the mitoses in the onion roots with a variation of not more than 10 per cent, have been proved incorrect, and it is considered by many authorities that when adequate controls are applied no real evidence of the Gurwitsch effect may be found. (Professor Gurwitsch is well known for his studies upon dialectical Marxism and other branches of pure philosophy.) Against this, we must set the fact that it is in many cases practically impossible to detect, by the use of non-living agents, phenomena to which living matter is highly susceptible, and the possibility must not be neglected that the radiation is too feeble for recording by physical methods although capable of considerable action upon more sensitive detectors such as cells and primitive organisms. At present, we can only suspend judgment upon the matter, and those requiring further information are referred to the Bibliography [481, 482].

The Photosensitized Decomposition of Nitrogen Trichloride.

The very high quantum efficiency observed in numerous photochemical reactions is due to the inception of a chain mechanism whereby energy liberated in the first stage is utilized in producing subsequent changes. The classical example of this is, of course, the

interaction of hydrogen and chlorine, which involves the sequence :



and the length of the chain is a measure of the joint probabilities (a) that the hydrogen or chlorine atom will not find the proper partner for the next stage, and (b) that the energy set free in any one process will be dissipated in some manner which does not involve chemical reaction. At the high pressures generally employed, the first of these factors is of very small account, and the second really amounts to the chance that the reaction chain will terminate close enough to the wall for a surface deactivation process to take place. In other reactions, however, deactivation of an energy-rich molecule in the gas phase becomes very important, as is well illustrated by recent studies by Norrish and his school upon various aspects of the hydrogen-chlorine reaction, which is now, largely through his admirable work, fairly completely analysed.

Following upon the proof that the induction period in the reaction is due to the formation of nitrogen trichloride, which has to be eliminated before the HCl synthesis proper can proceed [381, 382], Norrish has investigated [383, 384] the photochemical decomposition of NCl_3 in chlorine with $\lambda = 4360$ and 3650 \AA , and finds (a) that the reaction is photosensitized by the carrier gas, (b) that the process is of zero order with respect to the NCl_3 until just before all of the chlorine has become used up, when it becomes semi-explosive, and (c) that the quantum efficiency γ decreases with increasing chlorine pressure to a limiting value of ca. 2, the result being reproduced by the equation :

$$\gamma = \frac{1}{0.0038[\text{Cl}_2]} + 2.5.$$

No wall reaction as such is to be found [384] although with matured vessels, whose surfaces are covered with an invisible film of ammonium chloride, the value of γ is abnormally high due to suppression of the heterogeneous process and the consequent establishment of constant conditions in the gas phase. The diminution in γ which accompanies increase in the pressure of chlorine ($[\text{Cl}_2]$) clearly suggests that while this gas can initiate the reaction, it can also act inimically towards the chains, and exactly the same general effect is to be observed when the reaction is carried out in the

presence of inert gases (X), where γ is expressed by the equation :

$$\gamma = \frac{1}{0.0038[\text{Cl}_2] + k_x[\text{X}]} + 2.5$$

X denoting the inert gas and k_x the proportionality constant, characteristic for the individual gas concerned. The values of k_x represent "the relative depressing effects of the different gases" (Norrish), i.e. their efficacies as inhibitors of the chain reaction, and it is of great interest that here they fall in the same general order as is found for the "inert gas effect" in retarding the photochemical decomposition of ozone [385, 400] (Table 10 (b)), catalyzing the recombination of bromine atoms [386] and quenching fluorescence in mercury [108], sodium [115], iodine [387] and nitrogen dioxide [272, 388; cf. also 390].

TABLE 10 (a)

| Gas. | k_x |
|--------------------------|---------|
| Helium | 0.00093 |
| Argon | 0.0016 |
| Nitrogen | 0.0017 |
| Oxygen | 0.0025 |
| Carbon dioxide | 0.0038 |
| Chlorine | 0.0038 |

TABLE 10 (b)

| Gas. | Inhibition Effect in Ozone Decom- position [385]. |
|---------------------------|---|
| Helium | 0.13 |
| Argon | 0.22 |
| Nitrogen | 0.28 |
| Oxygen | 1.00 |
| Carbon monoxide | 0.62 |
| Carbon dioxide | 0.80 |

The limiting value for $\gamma = 2$ reached with high partial pressures of the inert gases is, as suggested by Norrish, very much in favour of the notion that they stabilize, probably in a termolecular collision of the second kind, an energy-rich complex such as NCl_4 , which is associated with chain rupture. It does not seem likely that the "quenching effect" here can be spurious and due to pressure broadening of the incident line, since the energy-resonance between both $\lambda = 3650$ and $\lambda = 4360$ is so small (D for $\text{Cl}_2 = 56.87$ Cals. $\equiv 2.47$ V) that this disturbing factor would be of little or no account. But it is curious that monatomic argon should be practically as effective as nitrogen, which is so rich in low vibrational states wherein it can absorb energy (cf. p. 84).

The Interaction of Hydrogen and Oxygen.

Both the photochemical [450, 451, 465, 466] and thermal [463, 464] combinations of hydrogen and oxygen have been the subject of much research in recent years, and although the former has many points of interest they are not strictly germane to the scope of this monograph and hence will not be discussed. Those desiring detailed

information are referred to the Bibliography. The latter reaction does, however, illustrate several very important aspects of the influence of collisions of the second kind, and will be treated at some length. Much important work is to be credited to Hinshelwood and his school at Oxford, and the composition of an account of their researches has been greatly facilitated by the brilliant monograph recently published by Hinshelwood and Williamson [447].

The reaction $2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O}$ at atmospheric pressure has long been known to proceed either with explosion in the gas phase or quietly at a surface, according to the conditions of experiment. In 1928, however, Hinshelwood and Thompson [448] found that in the temperature range ca. 460–600° C. there is a definite pressure region wherein the reaction is explosive, whereas both below and above these limits it proceeds quietly, if with some complexity, as a wall reaction. The combination is thus divisible into three well-marked zones, i.e. the quiescent high-pressure reaction, the low-pressure explosion, and the quiescent low-pressure reaction, as follows (Fig. 19).

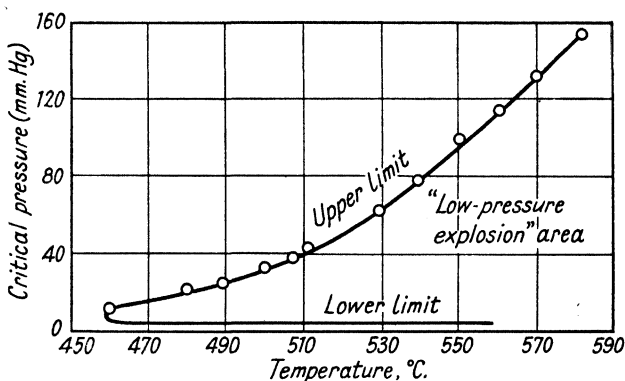
(a) *High-pressure Reaction* [cf. 448, 449, 447a]. At ca. 150 mm. total pressure (100 mm. H_2 , 50 mm. O_2) the velocity of reaction at ca. 550° C. is very small, but compression, or a slight increase in temperature, enhances it very considerably, e.g. for 559° C. the time of half change is 73 mins. at 300 mm., but ca. 7 mins. at 600 mm., to quote from one of Hinshelwood and Thompson's observations [448]. The reaction is autocatalytic, being accelerated by steam, which has however no specific properties since other gases act in a similar manner and fairly in proportion to their concentrations; their effectiveness lies in the order:



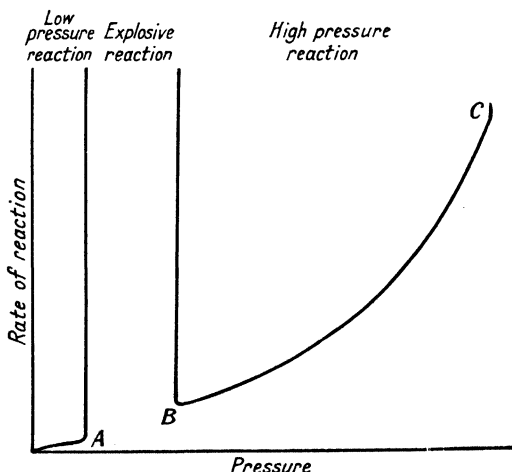
Introduction of glass or quartz tubing slows up the reaction, but if this material be then cut up into small pieces, or replaced by finer fragments of the same total volume, there is little or no effect. Similarly, the rate of the reaction varies very closely as the square of the diameter of the bulb, showing that we have to deal not so much with surface effects as such, but with something which accompanies a diminution of free space in the reaction vessel.

(b) *Explosive Reaction, at Low Pressure*. Although below ca. 150 mm. pressure the velocity of reaction in a hydrogen-oxygen mixture at 400–500° C. is very slow, explosion occurs if the pressure be even slightly reduced. The upper limit of pressure for this reaction is very much better defined than the lower, is independent

of both the diameter of the reaction vessel and the nature of the surfaces, and is lowered by addition of foreign gases [452, 453, 455]. The lower limit is harder to reproduce, but is also susceptible to foreign gases, as before.



(a) Explosion Limits in the Hydrogen-Oxygen Reaction (Hinshelwood and Williams).



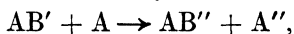
(b) Rate of Reaction as Function of Pressure (Hinshelwood).

FIG. 19.

Hinshelwood has shown that both the high-pressure and the explosive processes may receive satisfactory metrical interpretation if it is assumed that they are essentially chain reactions, the detailed mechanism being variable with the conditions of experiment [447b]. The principles involved may best be illustrated by reference to a

hypothetical reaction between molecules A and B, whereby the first stage is an activated AB complex: $A + B \rightarrow AB'$. This then imparts energy to another A or B: $AB' + A(B) \rightarrow AB + A'(B')$ which then becomes able to react *per se*: $A'(B') + B(A) \rightarrow AB'$, a reaction chain commencing and terminating either through some collision in the gas phase which is unfavourable to the requisite energy transfer, or in a deactivation process at the walls of the reaction vessel. Such a mechanism will provide for the large kinetic "order" of the high-pressure reaction, its dependency upon the free space available for propagation of the chains and the catalytic action of foreign gases by impeding diffusion of the active centres to the walls.

At lower pressures, however, a further possibility enters. Under these conditions, where the chance of a termolecular collision is so much smaller, or where it is less probable that the frequency of impacts will lead to degradation of small amounts of the activation energy with which AB' is initially endowed, a process:



may occur, both AB'' and A'' having sufficient energies to initiate further chemical change, so that there is an extremely rapid exponential increase in reaction velocity and explosion occurs. This represents the "chain-branching" effect originally advocated by Christiansen and Kramers [454] and later developed by Semenov [455] to account for the explosive interactions of oxygen and phosphorous vapour.

Finally, if the total pressure is so low that the activated AB' , or its products AB'' or A'' , diffuse to the walls and lose their energy before encountering other bodies towards which they are potentially reactive, the process will occur quietly with the formation of only short reaction chains. The combination of hydrogen and oxygen proceeds in this manner. The high-pressure reaction corresponds to the controlled chain process, the explosive stage to the branching chain process and the low-pressure reaction to another sequence of events wherein the propagation of chains is kept in check by wall destruction of their initiators. (This last represents the third type (p. 109).)

Consideration of the precise mechanism, and the nature of the reactive species, will for the moment be deferred.

Sensitization of the Hydrogen-Oxygen Reaction [447c, 459]. Both the high-pressure reaction and the explosive combination of hydrogen and oxygen at lower pressures are extremely susceptible to

traces of some foreign gases, notably the halogens and nitrogen peroxide. Addition of ca. 10^{-2} mm. of iodine or bromine will reduce the velocity of the non-explosive chain reaction at 550°C . and 450 mm. to about one-fourth of its original value, but chlorine is not quite so potent [456]. Similarly, the region of the low-pressure explosion may be much reduced, or even totally eliminated, by bromine or iodine present in concentrations of ca. 10^{-4} , or by 2.5×10^{-3} parts of chlorine. Hinshelwood considers that the action of the halogens is probably not hard to explain, because of their extreme reactivity towards substances which, since their deliberate addition from outside sources influences the nature of the reaction, may be assumed to participate in the chain processes. For example, iodine may react: $\text{I}_2 + \text{H} \rightarrow \text{HI} + \text{I}$, and the lower efficacy of chlorine in inhibiting both the high-pressure and the explosive reactions may be due to $\text{Cl}_2 + \text{H} \rightarrow \text{HCl} + \text{Cl}$, $\text{Cl} + \text{H}_2 \rightarrow \text{HCl} + \text{H}$, the hydrogen atoms—assumed to be important members of the chains—thus being regenerated.

It is certain that atomic hydrogen can strongly affect the course of the reaction, since addition of ca. 10^{-4} per cent H will lead to explosion of a mixture at 300°C . as compared with the 450°C . requisite, *ceteris paribus*, in the absence of the atoms [460, 461]. Semenov [461] considers that the hydrogen atoms here enhance the probability of chain-branching and thus expand the limits of the low-pressure explosion region.

Atomic oxygen is even more effective, the upper limit of the low-pressure explosion zone being moved so far along the pressure axis (Fig. 19*b*) that violent reaction occurs at almost any pressure to the right of the normal boundary [461].

The action of nitrogen peroxide has been the subject of considerable controversy. Hinshelwood and Thompson observed [457, 462] that at temperatures in the region of 400°C ., and under pressures where the reaction will normally proceed only very slowly, explosion may be induced by addition of nitrogen peroxide between two sharply defined limits of concentration, above and below which there is no appreciable sensitization. Norrish and Griffiths showed, on the other hand, that if the reaction vessel were modified by provision of an axial inlet tube, thereby diminishing the amount of free space, no explosion occurs, but merely rapid reaction, which may be accelerated by illumination of the mixture by light in the region $\lambda\lambda = 4360\text{--}4050$, where nitrogen peroxide is photochemically decomposed to NO and O [388]. In the absence of the axial tube,

irradiation has no effect upon the ignition temperature, explosion taking place in a normal manner [488]. Hinshelwood at first supposed that the NO_2 acts in this reaction both by initiating and breaking chains, the latter process, involving interference with hydrogen peroxide in an excited condition, being of much the same order of magnitude as the former, so that we may readily account for the limited range of concentrations over which the sensitizer is effective [457]. Norrish on the other hand [458] preferred a chain mechanism, also involving free radicals and similar unstable intermediate products, but depending primarily upon oxygen atoms, produced thermally or photochemically, and removed either by further reaction with NO_2 or by recombination upon the walls of the apparatus. With the further assumption that ignition shall occur when the velocity of reaction exceeds a given maximum, i.e. when the rate of generation exceeds the rate of loss of heat from the system, so that the process becomes adiabatic, Norrish was able to explain both Thompson and Hinshelwood's [457] and his own [458] observations.

Hinshelwood, however, [447*d*] points out that the above mechanism would presuppose a photochemical ignition, which does not occur; suggesting therefore that the reaction involves chains starting from a body X and uniting with NO_2 to give some substance Y capable of inducing further branching, or of being deactivated by the intervention of yet another NO_2 molecule, he obtains an equation which accounts for some of the experimental observations such as the upper and lower limits of ignition as a function of the concentration of nitrogen peroxide.

The latest work by Foord and Norrish [459] seems to effect a considerable synthesis between these conflicting theories. They consider that Hinshelwood's scheme does not recognize (a) the homogeneous reaction which proceeds outside the explosion limits, (b) the conversion of an explosive to a non-explosive, albeit fast, reaction, which accompanies increase in the surface of the apparatus, and (c) the disappearance of the lower limit of ignition at high temperatures, although the upper limit remains. Very comprehensive experimental researches show that nitrogen peroxide acts as a catalyst for both slow and explosive reaction, its effect passing through a maximum and then falling away to nothing as its concentration is increased; the lower limit of concentration, if it exists at all, is certainly less than 0.01 mm. in a mixture at 350°C . (Fig. 20). Both reactions are subject to an induction period, which varies

continuously with concentration of NO_2 and is at its minimum where the catalytic effect is at its greatest. Irradiation with light which will decompose NO_2 markedly enhances the velocity of the slow reaction, while the induction periods of both slow and explosive reactions are reduced from 20 to 500 seconds to less than one second; the limits of the ignition region remain, however, unaffected by irradiation, although they may be much reduced, or even suppressed, by increase in the surface: volume ratio of the apparatus, by increase of the pressure of oxygen, or by addition of foreign gases,

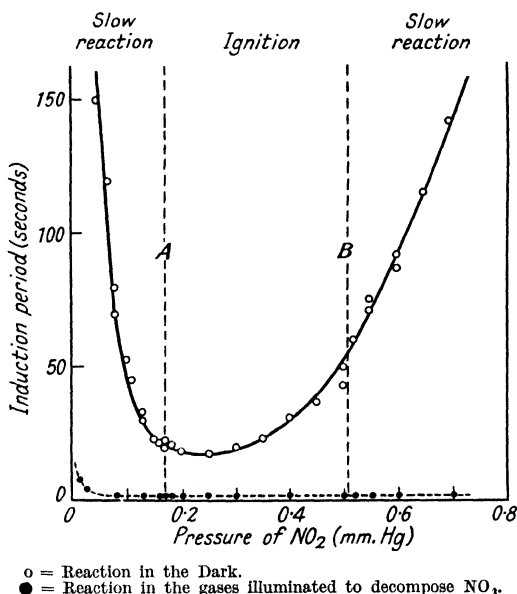


FIG. 20.—Effect of NO_2 on the Combination of Hydrogen and Oxygen (Foord and Norrish).

methane being remarkably effective in this respect. All of these observations may well be explained by a modification of the earlier theory of Norrish and Griffiths. It is now supposed that the reaction proceeds from active centres derived initially from nitrogen peroxide. Although their concentration in the beginning is small, they undergo an exponential increase in numbers during the induction period, until a stage is reached when their production, both *per se* and by chain-branching, is counterbalanced by destruction both in the gas phase and at the walls. Their maximum concentration in an element of volume thus being dependent upon a

factor which will vary both with the nature and the distance of this element from the walls, it is clear that at some instant their number n may be so great as to convert an approximately isothermal reaction into an adiabatic one, with consequent ignition of the gas mixture. But since this optimum concentration n_c will be determined (a) by the rate of production of chains in the primary process and (b) the effective branching factor ϕ , i.e. the difference between the probabilities of branching and deactivation apart from self-neutralization, which is itself a function of the concentration of nitrogen peroxide, it follows that there will be upper and lower limits to the pressure of NO_2 for explosion, an upper limit to the pressure for *any* kind of catalytic action, but no lower limit to the amount which can affect the slow reaction, all of which deductions have been verified.

Irradiation of the mixture by light which dissociates NO_2 to NO and O practically eliminates the induction period by enhancement of the primary reaction, but does not affect the explosion limits since it has no action upon the effective branching factor; but when the surface: volume ratio is sufficiently increased, ϕ , which contains a surface deactivation factor, may become so much reduced that the requisite value for n_c is never attained, i.e. ignition is suppressed although rapid reaction may still occur in what Semenov has termed a "degenerate explosion" [cf. 447e].

The condition for ignition is thus that there should be a breakdown of thermal deactivation by collisions of the second kind, and Foord and Norrish have obtained very interesting evidence that this does actually occur. To quote from their paper:

In the region just outside the ignition limit it is seen that the induction period is terminated by a sharp pressure increase followed by a fast reaction, which slows up considerably to a steady value in the course of a minute or so. Since the reaction itself occurs with a fall of pressure, the sharp increase of pressure terminating the induction period is clearly a heat effect, and marks the tendency of the reaction to become adiabatic at this point. The particular form of the curve leads one to believe that we are here witnessing an incipient thermal ignition in some favourable volume element, which rapidly dies away as the reactants in the element are consumed. The process once more becomes isothermal and a steady reaction velocity ensues.

Initiation of the reaction chains would almost certainly appear to be effected by atomic oxygen. Apart from the direct evidence obtained by Norrish as to the irradiation of the sensitized mixture [458, 459], the thermal process alone may well permit of

$\text{NO} + \text{O}_2 \rightarrow \text{NO}_2 + \text{O}$, since the dissociation of NO_2 to NO , even in the presence of excess of oxygen, will be quite appreciable at ca. 300°C . and over. This last reaction is also very probable in a collision of the second kind with the actual hydrogen-oxygen chain.

We may, for the sake of completeness, conclude this section with some considerations upon the nature of the main reaction chains and their place of origin. As Hinshelwood points out, it is frequently possible to obtain convincing explanations as to the kinetics of a reaction with the minimum of assumption as to the nature of the actual participants. This fundamental weakness of the thermodynamic method is very dissatisfying to those desiring a more complete understanding of the train of events in such processes, and it is a matter for congratulation that spectroscopic and photochemical studies have in recent years done much to rectify such a serious defect.

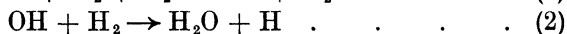
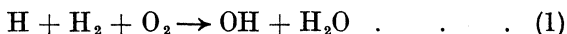
At one time an active steam molecule $\text{H}_2\text{O}'$ was regarded as the originator and propagator of the reaction chains, but this view has now largely been abandoned (a) because of the high general efficacy of water vapour as a *deactivator* in collisions of the second kind and (b) by reason of the absence of any apparent quenching effect of foreign gases upon the reaction. Hydrogen peroxide or the radicals OH and HO_2 would seem much more likely to be of importance.

The first named may readily be obtained in quantity by the action of atomic hydrogen upon oxygen [467], and it has been shown both by Haber [460] and by Semenov [461] that hydrogen atoms can very markedly influence various stages of the reaction, especially the low-pressure explosion. Pease has also found [468] that when a 2 : 1 mixture is allowed to react at $520\text{--}550^\circ \text{C}$. in clean Pyrex vessels, the combination is rapid with formation of hydrogen peroxide in quantity up to $1 \text{ H}_2\text{O}_2 : 4 \text{ H}_2\text{O}$, whereas when the walls are covered with a thin film of potassium chloride, the velocity of reaction is reduced to ca. $1/500$ of its original value and water is the only product. While this observation may indicate that an $\text{H}_2\text{O}_2'$ undergoes a stabilizing deactivation at glass but not at KCl surfaces, other possibilities may be of as much import [cf. 447f].

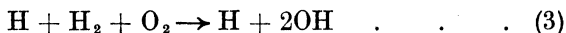
Direct evidence as to the possible rôle of the hydroxyl radical is conflicting. It is certainly formed in the dissociation of steam at ca. 1200°C . and spectroscopic evidence recently presented by Oldenburg [469] suggests that its life period may be very considerable although measurements by Bonhoeffer and Pearson [470] seem to show that it very readily reacts: $2\text{OH} \rightarrow \text{H}_2\text{O} + \text{O}$, and that,

at any rate in the discharge, it is very unstable [cf. also 472]. If, however, it can persist for any considerable period, no mechanism can be complete which does not take cognizance of this fact.

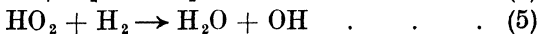
The oxide HO_2 would appear to be of much importance in the photochemical reaction between hydrogen and oxygen [cf. 451, 447g], but a fuller discussion of this point is beyond the scope of the present work. It may suffice to state that the mechanisms which seem to provide the best correlation between the modes of combination of hydrogen and oxygen under various conditions are essentially modifications of that proposed in the first instance by Haber and now known by his name [463, 464]. It is :



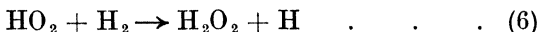
Reaction 1 may sometimes take the form :



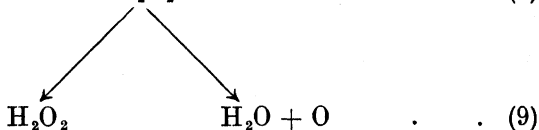
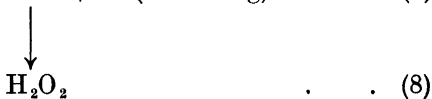
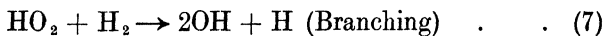
which accounts for the branching of the chains. Hinshelwood and Williams [447b] suggest that since the initial ternary collision will be of infrequent occurrence, it should be divided into :



stage 4 occasionally proceeding as :

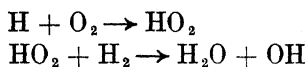


which is preferable for the normal photochemical reaction. This scheme also has the advantage that it provides both for branching and the formation of hydrogen peroxide :

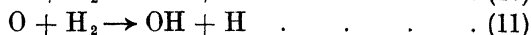


depending upon experimental conditions. It is furthermore able to account (a) for the energies of activation which are observed and (b) the enhancement of branching, and widening of explosion limits, by atomic hydrogen and oxygen (*vide supra*).

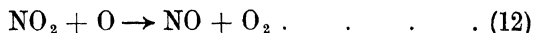
Foord and Norrish [459] advocate :



with :



to account for the chain-branching. Breaking of the chains by nitrogen peroxide may involve :



The place of origin of the chains is not definitely known, this problem having so far eluded direct experimental investigation. The various reaction schemes seem equally applicable according as we suppose either that the chains commence in the gas phase and undergo rupture at walls whose efficacy in this respect will naturally be widely variable, or that they commence upon surfaces whose ability to retain the active centres will similarly alter from case to case. The balance of evidence, however, seems to point to the walls as their source [cf. 447*f*, 447*i*].

The most direct suggestions are due to Alyea and Haber [473]. They allowed streams of hydrogen and oxygen, separately heated to ca. 400° C., to meet in a large vessel to which nitrogen and other gases were added as diluents, the pressure being maintained by pumps so that the mixture was held well within the low-pressure explosion region. No ignition occurred in this case, but when rods of quartz, glass, porcelain, copper or iron were inserted at the point of confluence, a flame immediately appeared, only to vanish with removal of the surfaces.

Aluminium had no effect. Additional evidence in the same direction is provided by observations (*a*) that pre-treatment of a porcelain tube by hydrogen narrows the low-pressure explosion limits [473] and (*b*) that steam—which is, of course, very strongly adsorbed—has a strong inhibiting effect upon the same process [456].

The Thermal Decomposition of Nitrous Oxide.

We have already seen that the quenching of resonance radiation by a foreign gas is in many cases closely bound up with the ability of the diluent to take up energy in its lower states of excitation. This is, of course, tantamount to an activation of the molecules involved, but, as we have already seen, an exact interpretation of

the mechanism is hard to come by because of disturbing factors which may, in some cases, very largely mask the process which it is desired to study.

Indications as to an alternative line of attack are, however, developing from a very important series of investigations made by Volmer and his school upon the homogeneous thermal decomposition of nitrous oxide. Their studies derive in the first instance from various well-established observations as to the change in the order of some gas reactions as the pressure is varied. The decomposition of dimethyl ether is, for example, bimolecular at low pressures, but at higher pressures, unimolecular. According to Hinshelwood and Askey [483] to whom the result is due, this indicates a high activating power of one ether molecule towards another, so that at high pressures of the reactant, or in the presence of other gases, such as hydrogen, which can produce the same effect, the molecule is virtually kept, through the agency of collisions, in an activated state for a time interval adequate for spontaneous decomposition. At lower pressures, or with addition of gases of low activating power (e.g. methane, helium, nitrogen), this process is not possible and reaction takes place as a bimolecular change according to the ordinary classical picture [cf. 484].

Volmer and his collaborators start from considerations advanced by Rice and Ramsperger [396 ; see also 397] in their well-known paper upon activation in gas reactions, according to which the molecules which decompose are those which after collisional activation remain associated with internal energy contents and free life periods which are not invariable over a wide range of conditions, but are susceptible to the pressure and, of course, temperature. The reactive bodies are those of energy $\bar{E} = E_0 + 3kT$, where \bar{E} is related according to the Maxwell law with E_0 , the energy required for the rupture of a particular linkage (here the $N_2 - O$ bond) and k is Boltzmann's constant. Their mean life period may be calculated from the experimental results as ca. 10^{-10} sec., which agrees fairly well, in view of the assumptions inherent to the theory, with that evaluated from equations due to Frenkel [398] and Polanyi and Wigner [399] whereby τ is connected with E_0 and the highest fundamental frequency of the N_2O molecule, which is known from spectroscopic data. The heat of dissociation of oxygen thus derived (154 Cals. \equiv 6.7 V) does not, however, agree so well with that now accepted (117 Cals. \equiv 5.17 V).

Now the mean life period of the active molecules increases with

falling pressure p since those of long life contribute more to the reaction than at high pressures, where the time interval between collisions is too short to enable them to react, and for low values of p the plot of $\frac{1}{p}$ against $\frac{1}{k}$, which for unimolecular reactions is linear with intercept upon the $\frac{1}{k}$ axis at p_∞ (k being the velocity constant) consequently bends over towards the axis of $\frac{1}{p}$ (Fig. 21).

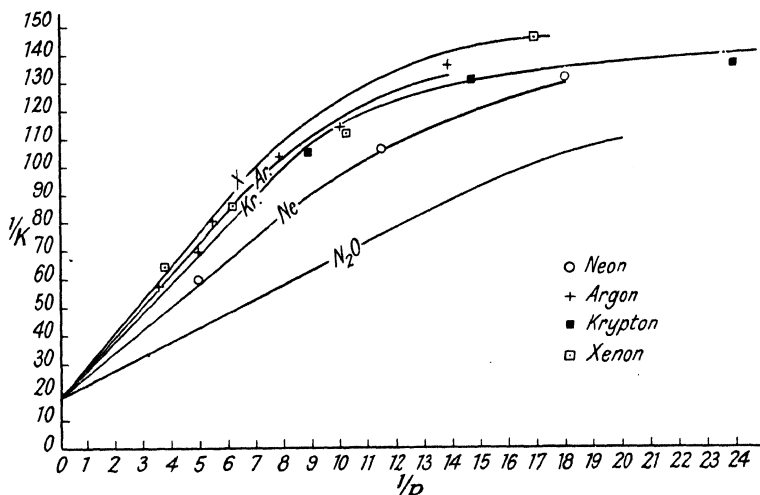


FIG. 21.—Activation by various Gases in the decomposition of N_2O (Volmer *et alia*).

The fraction of reactive N_2O' molecules clearly being constant for any one value of p , we may write :

$$\frac{1}{k} = \frac{1}{k_\infty} + \frac{B}{P_n} \quad . \quad . \quad . \quad (1)$$

(for reactions in pure N_2O)

$$\frac{1}{k_f} = \frac{1}{k_\infty} + \frac{B}{x.p_f + p_n} \quad . \quad . \quad . \quad (2)$$

(for reactions in the presence of foreign gases),

B being a constant and x the probability of activation by collision with the foreign gases at equivalent pressures. Expressing the

partial pressures p_f (foreign gas) and p_n (nitrous oxide) as percentages of the total pressure P , we have :

$$x.p_f + p_n = P\left(\frac{x.a}{100} + \frac{b}{100}\right) = Px' \quad . \quad . \quad (3)$$

x' being the mean probability of activation in the gas mixture.

From this it follows that :

$$\frac{1}{k_f} = \frac{1}{k_\infty} + \frac{B}{x'P}.$$

Now if P_n represents a pressure where a given departure from linearity in the graph occurs for the reaction in pure N_2O , this same effect should appear with a gas mixture at pressure P where a long-lived N_2O' has the same chance of decomposition as in the first case. The points concerned cannot all lie at the same pressure, since although the collision frequencies will be equal, the chances of deactivation are different, being in the first equal to unity, and in the second to x' . If $x < 1$, then $P > P_n$, increasing with diminishing values of x' , i.e. :

$$P = \frac{1}{x} . P_n, \text{ or } x' . P = P_n \quad . \quad . \quad . \quad (4)$$

On substituting these values in equation (4), we have $k = k_f$, i.e. for equal velocity constants equal departures from linearity in the graph should be observed, the actual inflexions starting in all cases

at $\frac{1}{k} = 100$ to 110 and

$$\frac{P_n - p_n}{p_f} = x \quad . \quad . \quad . \quad (5)$$

TABLE 11

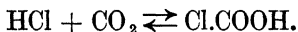
ACTIVATION OF NITROUS OXIDE BY IMPACT WITH OTHER MOLECULES (Volmer)

| Foreign Gas. | Probability of Activation per Collision = x . | Activating Impacts. |
|--------------------------|---|---------------------|
| | | Total Impacts. |
| Water vapour | 1.5 | 1 : 127 |
| Carbon dioxide | 1.32 | 1 : 145 |
| Nitrous oxide | 1.00 | 1 : 190 |
| Nitrogen | 0.24 | 1 : 800 |
| Oxygen | 0.23 | 1 : 830 |
| Helium | 0.66 | 1 : 290 |
| Neon | 0.47 | 1 : 400 |
| Argon | 0.20 | 1 : 935 |
| Krypton | 0.18 | 1 : 1050 |
| Xenon | 0.16 | 1 : 1160 |

Such considerations are clearly invalid where there is definite catalysis of the reaction by the foreign gas, which can be detected—as for example with the addition of iodine or bromine—by alteration in the energy of activation, but Table 11 shows the variation in the yield of “active” N_2O molecules obtained by collision with sundry gases, referred to x for N_2O as unity.

Here, as in the parallel, if inverse case, of the deactivation of optically excited mercury and other atoms, the various gases are highly specific in their action, although as regards probability of excitation per impact as a function of molecular mass, the elementary gases all lie on the same curve, the slight departure of krypton from this regularity being attributed, by Volmer, to the accidental presence of a trace of water vapour. It is also noticeable that above ca. 40, the atomic weight has little influence upon x , although the ratio (fruitful impacts)/(total impacts) steadily decreases.

Eucken and Becker [355] have made semi-quantitative studies upon the effects of gases such as methane, hydrogen chloride, and the noble elements, upon chlorine and carbon dioxide excited by ultrasonic waves ($3 \cdot 10^5$ Hertz), and consider that in many cases the ability of one gas to activate another by conversion of translatory into vibrational energy, is best explained by reference to forces of a chemical rather than a physical nature. They suggest that gases with negligible dipole moments (e.g. H_2 and CH_4) distort the potential function of the target molecule both by a process of electrostatic attraction, and also through the agency of quantum-mechanical interchange-forces, whereas others may give rise to quasi-molecules of short duration:



Helium is very effective, in spite of its tightly bound electron structure, because of its ability to penetrate well into the field of the other body concerned.

The process thus acquires a certain parallelism with that of electronic excitation, which nowadays is considered by some authorities to be best amenable to treatment in terms of resonance rather than by the older impact theory. Evidence has for some time been available that slow electrons can excite low vibrational states in some molecules such as CO and N_2 [486] and H_2 [487]. This may mean, according to Franck and Jordan [490], that the projectile electron partially enters into the electron system of the target molecule, and thus affects the nuclear binding forces. The disturbance of the electron shell being essentially adiabatic, the

potential energy conferred upon the molecule appears as vibrational energy of the nuclei. The effects are thus much greater, for a given electron velocity, with the polar CO molecule than with the non-polar N₂, in analogy with the strong and feeble infra-red absorptions which they respectively exhibit. Hydrogen, which is even more susceptible than nitrogen and carbon monoxide to such excitation of low energy states, does not really constitute an anomaly, since the temporary introduction of a third electron to its simple two-electron shell will naturally give rise to a greater disturbance than is to be expected in nitrogen or carbon monoxide, with their more complex structures. The subject is as yet so obscure that further discussion would not be of much value. Reference may, however, be made to the Bibliography [485, 488, 489].

The Deactivation of Acoustically Excited Molecules.

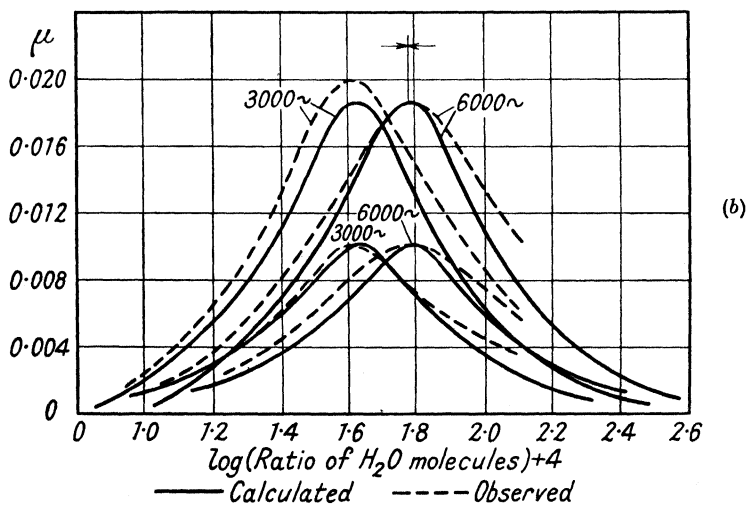
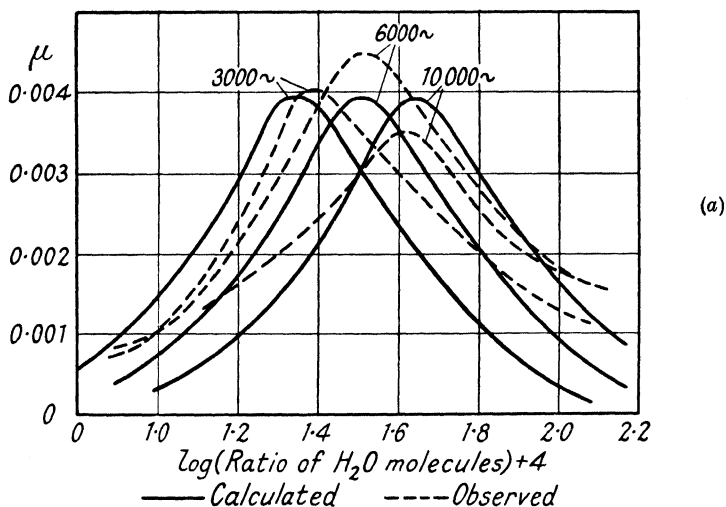
We may in this section digress somewhat from the main theme of the book, in order to consider briefly some recent investigations which bid fair to throw much light upon collision processes of the kind wherein we are interested in this chapter.

It has long been a source of regret to chemists that both the accuracies of electrical measurements, such as may be applied to the impacts of charged bodies, and the elegant, if occasionally somewhat optimistic conclusions of spectroscopy, are seldom applicable to those energy states wherewith he is most concerned. In most chemical reactions, the energy changes are of a low order (e.g. 1 to 3 V \equiv 20 – 70 Cals.) compared with those involved in the phenomena of ionization and most types of spectral excitation, and it is only of late that means have become available for the exploration of vibrational states of the ground electron levels of molecules. This has been rendered possible by the development of means for the generation and study of ultrasonic waves [cf. 258–260, 289].

It was discovered by Knudsen, in 1931, that the absorption of such waves by air is entirely in disagreement with predictions from classical theory, which demands that absorption due to heat conductivity and internal friction should vary as the square of the frequency and be but little affected by the purity of the gas, whereas in fact its magnitude is much greater than is to be expected, increases linearly with the frequency, and is markedly sensitive to moisture.

This anomalous absorption has been explained by Kneser [352, 353] in terms of collision theory, the basic mechanism being essentially quite simple. When a gas is adiabatically compressed, a

certain proportion of the work performed is converted into intra-molecular energy, which may be entirely regained upon expansion provided that both processes are carried out so slowly that the gas



(a) Air at 328° K; (b) Oxygen at 325° K and 293° K.

FIG. 22.

may be regarded as running through a series of equilibrium states. Should they be, however, performed in a time interval comparable with that necessary for the establishment of the thermal equi-

brium between the normal and the vibrating molecules, then some of the latter will be dissipated in raising the temperature of the gas, since their energy has not been liberated mechanically during the expansion. But if both processes are allowed to take place in a time interval very short relative to the period of adjustment of the equilibrium, no energy is converted into the internal form and hence no absorption from the outside source will occur.

† Now since alternating compression and expansion occurs when a sound wave passes through a gas it follows that there should be no energy absorption at very low or very high frequencies, but a

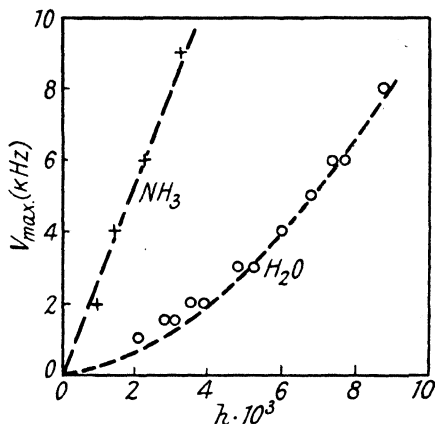


FIG. 23.—Effects of Impurities upon Absorption of Ultrasonic Radiation in Gases (Kneser).

maximum absorption when the interval between wave-crests equals the mean life of the vibrational quantum held by the molecules, i.e. ca. 10^{-6} sec. Kneser accordingly finds that ultrasonic waves in the region $3-6 \cdot 10^6$ cycles, obtained from a piezo-electric system [cf. 258, 352] exhibit very strong absorption maxima at frequencies which are most variable by the addition of foreign gases to that undergoing examination. Treating the process as a unimolecular reaction between vibrating and non-vibrating molecules which is harmonic with respect to time, he derives equations excellently in accord with observation both as to the magnitude of the absorption coefficient, and also the frequency where the anomalous absorption is at its greatest (Fig. 22). The shift in the absorption maxima towards higher frequencies which accompanies admixture of diluents, is due to the diminution which the impurities induce in the mean life of the vibrational state, and with many gases the frequency for optimum absorption is a linear function of the con-

centration of the foreign substance. With water vapour in oxygen, the curve is more quadratic in form, and Kneser suggests that this may be due to the high probability of deactivation of a vibrating oxygen molecule when it undergoes a termolecular collision with two water molecules (Fig. 23).

We have thus obtained a collisional quenching of just those states which are of most interest for the majority of chemical reactions, all measurements being made under conditions where troublesome factors such as pressure broadening and its analogues are completely absent. It is to be hoped that further studies upon these lines will soon be made, since their possible scope is clearly very great.

Collision Phenomena and Radiation in Explosions.

Considerations of the rôle of collisions of the second kind in preventing explosions by chain-rupture, etc., may fitly be succeeded by reference to observations, first made by Bone and his school, as to the remarkable effects of nitrogen upon the course of detonations in high-pressure mixtures of carbon monoxide and oxygen, and the later work which these discoveries have engendered.

The earliest data are illustrated in Fig. 24, and show that nitrogen quite selectively retards both the rate of onset and the rate of fall of pressure, and lowers the maximum pressure attainable. The pressure-decay curves for these explosions with various diluents are shown in Fig. 25, and it will be noted that the effect is confined to the one reaction, i.e. $(2\text{CO} + \text{O}_2)$, the hydrogen-air $(2\text{H}_2 + \text{O}_2 + 4\text{N}_2)$ explosion being quite normal as regards its pressure-time characteristics. The form of these curves leads inevitably to the conclusion that the nitrogen is able to absorb energy developed in the early stages of the reaction proper, and liberate it slowly during the subsequent proceedings.

Considerable evidence in favour of this hypothesis as to the genesis of an "activated" form of nitrogen is available, it being remembered that the variety concerned must almost certainly be quite distinct from the Strutt modification, which is essentially atomic in nature (cf. pp. 18-23). The principal facts are as follows:

(a) Formation of nitric oxide up to 6 per cent by volume may be observed, this substance appearing only during the cooling process, when the peak pressure has been passed. Attempts to account for its development in a purely "thermal" reaction, lead to the necessity for temperatures for which there is no justification on other grounds, notably the spectra of the explosion flame (*vide infra*), and the assumption of an active state of nitrogen provides a much better foundation for a mechanism of reaction.

(b) The data of Fig. 25 suggest a life period of ca. 0.6 second for the active state, which is not unreasonable were low vibrational or rotational states to be concerned (cf. pp. 84 et seq.). It has already been pointed out that the electrical synthesis of nitric oxide may readily be explained by a mechanism which involves, as one

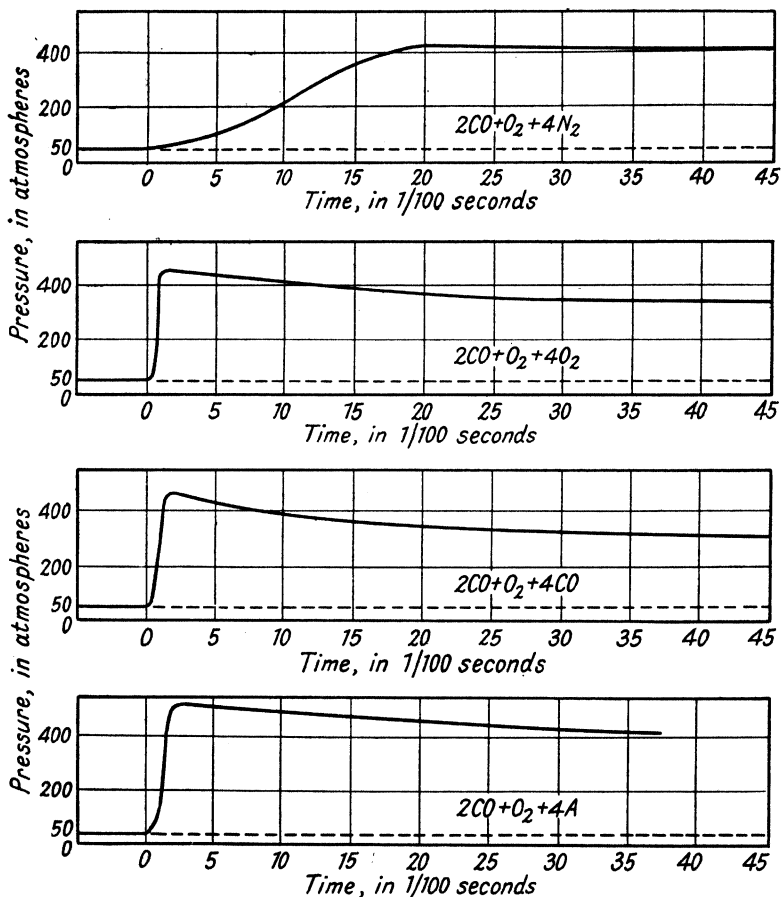
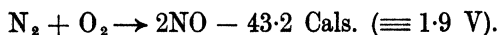


FIG. 24.—Activation of Nitrogen in $[2CO-O_2]$ Explosions (Bone and Townend).

of the reaction partners, a nitrogen molecule in a low state of excitation [503], and if we are prepared to assume that in the explosion only this element is activated, the vibrational levels $n \geq 7$ have energy enough to provide the 1.9 V requisite for the reaction :



(c) The radiation emitted by a ($2\text{CO} + \text{O}_2$) explosion in the absence of diluents, is strongly absorbed, over the region $\lambda = 3200\text{--}4400 \text{ \AA}$, if any excess of CO or nitrogen be present. This may mean, as Bone and Townend point out, that the reaction is photochemically autocatalytic, radiation emitted in the early stages being either absorbed to give further reactive CO molecules, or, if nitrogen be present, utilized in creation of an abnormal modification of this latter element. The higher the pressure, the greater then should be the magnitude of this absorption, owing to the enhanced probability

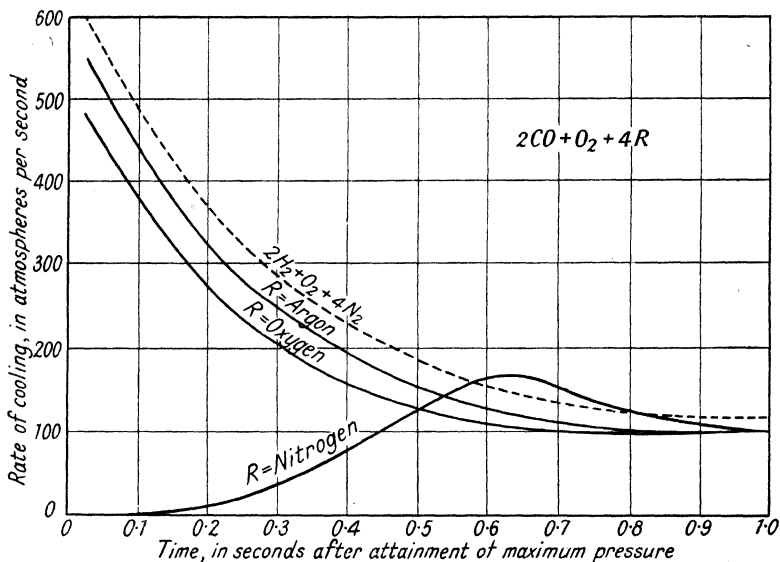


FIG. 25.—Activation of Nitrogen in [$2\text{CO} + \text{O}_2$] Explosions (Bone and Townend).

of interception of radiation, while a lower limit to the pressure range wherein the phenomenon is discernible, should correspondingly be anticipated, in agreement with observation. But since both nitrogen and carbon monoxide are quite transparent in this region, no absorption setting in before $\lambda = 1450 \text{ \AA}$ and $\lambda = 2064 \text{ \AA}$ respectively [501, 502], such a simple mechanism cannot be accepted. Fortunately, however, a number of observations upon the flame spectra of CO are at hand to indicate alternative methods of approach to the problem.

According to the extended researches of Weston [504], these spectra consist, under almost all circumstances, of a continuum upon

which is superposed a series of very diffuse bands, the whole ranging from approximately $\lambda = 2500$ to $\lambda = 5500$ Å.

Little is known about the continuum, but it may progressively be suppressed by addition of hydrogen, until in the flame of burning water gas it is no longer to be seen. Excess of oxygen is also unfavourable to its appearance. The bands are quite different from any of the other CO bands which appear in discharges,* and their intensity is enhanced by drying, or by reduction in the overall pressure. They also constitute the characteristic emission of the afterglow in carbon dioxide at low pressure, and since the spectrum

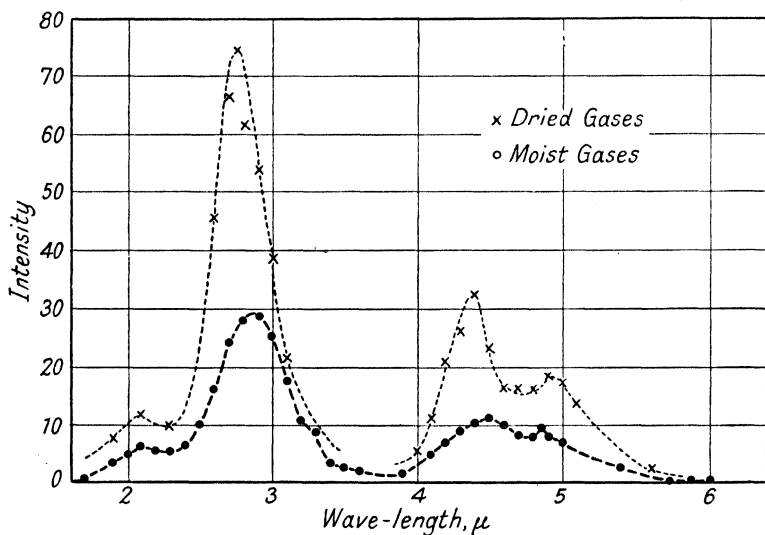


FIG. 26.—Effect of Moisture on the Radiation from a Carbon Monoxide Flame (Garner and Johnson).

of the discharge wherein they are here developed shows *only* bands such as the Ångström or Fourth Positive series, due to neutral CO, other groups deriving from ionized or atomic states being absent, it is to be concluded that they must represent a chemiluminescent interaction of neutral molecular oxygen and excited neutral carbon monoxide [508]. The consensus of opinion favours, as their emitter, a CO-oxygen complex which is in process of becoming CO_2 [506–508].

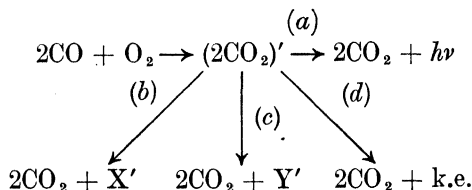
Evidence indirectly confirmatory that these flame spectra do not involve ionized states, in spite of the well-known prevalence of charged bodies under these circumstances [cf. 510], has been obtained by Kirkby from a study of the rates of decay (α) of the luminosity

* For an excellent summary of CO spectra, see [505].

and (b) the conductivity of a $(2\text{CO} + \text{O}_2)$ explosion. The light from the reaction zone was focussed upon a photocell, and the amplified photocurrent, along with the similarly amplified ionization current, applied to a two-element Dudell oscillograph, so that both processes could be followed simultaneously. The maximum conductivity and the greatest luminosity were found to occur at practically the same time after explosion, but the radiation was much more persistent than were the charged bodies; in a typical experiment, the conductivity fell by one-half in 0.01 sec., whereas the same reduction in the intensity of the light did not occur until 0.04 sec. Kirkby therefore concludes that ionization processes cannot account, to any appreciable degree, for the luminous phenomena of explosions, and that the charged particles have their origin in processes secondary to the main reaction. Since nothing is known as to the nature of the ions which appear in such cases, we cannot, however, neglect wall deactivation as a possible source (cf. Chapter IV).

Important studies upon the relations between reaction velocities and the infra-red spectra developed in the combination of carbon monoxide and oxygen, with especial reference to the influence of hydrogen and water and other substances, have been made by Garner and his school [511–518, 526]. Very small amounts of water reduce the intensity of the CO_2 bands at 2.8 and 4.4μ , but measurements upon the broadening of the latter indicate that the gases are much hotter here than in the corresponding reaction with dry gases. Reduction in the total radiation is accompanied by an increase in reaction velocity, an effect which can be obtained by the use of catalysts.

Garner and Johnson, to whom these observations are due, suggest that their data may very simply be explained by postulation of an activated complex which—depending upon the circumstances—can (a) radiate, (b) lose energy to other molecules, of the reacting species proper, in collisions of the second kind, (c) undergo quenching by foreign molecules if present, or (d) be caused, by these same molecules, to degrade their internal energy in the kinetic form. The process is thus:



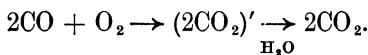
(X and Y respectively denote molecules of the chemically reacting species, and purely quenching agents.)

The formal distinction between the various types of energy loss are but small, but serve well to illustrate the effects observed. Reaction in the pure gases is described by processes (a) and (b); positive catalysts favour (b) and (d), negative catalysts stages (c) and (d).

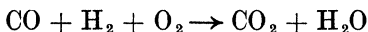
Hydrogen exerts a profound, but hitherto enigmatic, influence upon carbon monoxide-oxygen explosions. There is an abrupt increase in the velocity of high-pressure CO-air explosions when more than 0.6 per cent hydrogen is present, the (pressure, time) curve being so steep as to suggest a "knock" effect. It has not been possible to arrive at any definite conclusions as to the reasons for this phenomenon, but one possibility is a shortening of the pre-flame period by a "negative activation" process, energy which would otherwise be degraded, internally or externally, being maintained in a form whereby it can exert the maximum accelerating influence upon the explosion. Very probably an activated steam molecule is an important factor here, owing to the inception of another mechanism of reaction [516].

This suggestion derives from further observations by Garner's school [512, 515] as to the effects of hydrogen upon the infra-red radiation from a carbon monoxide flame. The CO₂ bands at 2.8 and 4.4 μ exhibit first a steady weakening in intensity as the concentration of hydrogen is increased, but at 0.03 per cent hydrogen there is an abrupt discontinuity over a short range, above which the regular diminution recommences.

It is considered that two definite mechanisms of flame propagation are here involved. In the first, traces of water are formed, and exert a normal quenching effect upon the (CO₂) complex:



At the critical pressure of hydrogen, this sequence is superseded by the process:

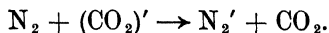


which is naturally different, in its radiative aspects, from the first reaction.

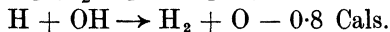
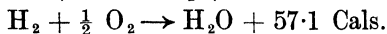
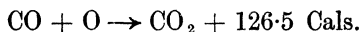
The notion of an activated CO₂ complex—which in fact considerably antedates the more precise *obiter dicta* of the spectroscopists—may be adopted to provide a simple explanation both of Bone's

nitrogen activation effect, and of other flame and explosion phenomena as well.

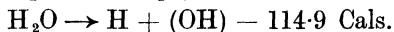
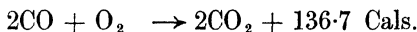
The genesis of the activated nitrogen follows from a collision of the second kind :



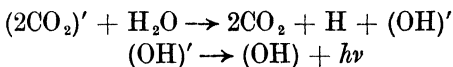
The same mechanism may be responsible for the appearance of the hydroxyl bands in the CO_2 afterglow when water is present [508] or in explosions of wet $\text{CO} - \text{O}_2$ mixtures. Taking for the heats of reaction [517] :



we may calculate :



whence it follows that were a $(2\text{CO}_2)'$ complex, holding its heat of formation, as given above, to collide with a molecule of water, the latter could be dissociated to atomic hydrogen and hydroxyl. Since the transition associated with the hydroxyl band ($^3\Sigma \rightleftharpoons ^3\pi$) at $\lambda = 3064 \text{ \AA}$ requires however 92 Cals. $\equiv 4.0 \text{ V}$, [524] a process :



is not possible, but in view of the very high temperatures developed in the explosion, a thermal dissociation of water is quite likely, followed by excitation of the hydroxyl upon impact with the active complex. Where a discharge is concerned—as in the case of the carbon dioxide afterglow—primary formation of the hydroxyl could easily occur as an electrical effect [cf. 519, 520] with secondary excitation as indicated.

Partial suppression of the normal radiation from the $(2\text{CO} + \text{O}_2)$ explosion by excess of CO may also be accounted for as a quenching process which leads to a degradation of the internal energy by conversion to the kinetic form, no active state of CO being formed, in distinction to the parallel reaction with nitrogen.

A note upon the nature of the flame spectrum of CO may here not be out of place. The continuum is a characteristic of burning CO only, as it does not appear in the flames of hydrocarbons. In this latter case, the only spectra are those due to the radicals (CH) and (OH) , i.e. the methine and hydroxyl bands, together with the

Swan bands of carbon, due to (C.C). Continua, which indicate the emission of unquantized radiation, are in general associated either with recombination or with dissociation reactions. The former case may be exemplified by the process of ion-neutralization, where the equivalent of the ionization potential, unordered kinetic energy of the electrons must be added; we have thus transitions from a large number of upper states to a common lower one. Dissociation, as for example by optical absorption beyond the convergence limit, represents the converse process wherein transitions occur from one lower level to a multiplicity of upper states.

There would seem no reasonable *a priori* grounds for attributing the CO flame or explosion continuum to a process of ion-neutralization although a very simple test could be made by following any changes in conductivity occurring in flames of constant mean temperature, but dosed with increasing amounts of hydrogen to suppress the particular spectrum concerned. An alternative dissociation reaction is equally hard to envisage, so there would so far appear to be no solution to the problem.

Collisions of the Second Kind in Liquid Media.

We may conclude this chapter by reference to some recent researches which seem to show that the general principles already discussed, albeit mainly for gaseous systems, are equally applicable to liquid systems. Before Franck's generalized theory received full recognition much ingenuity was fruitlessly expended in attempts to account otherwise for some of the optical phenomena of solution, notably that photo-processes here usually exhibit a greater degree of departure from Einstein's law than is observed for reactions in the gas phase. Weigert, for example, supposed that one such case, i.e. the formation of *o*-nitrobenzaldehyde from *o*-nitrosobenzoic acid, involves first the transfer of an electron from the aldehyde-group, consequent upon the absorption of light, but that actual reaction occurs, with migration of an oxygen atom, only when the electric vector of the incident radiation is co-linear with the chemical bond between the groups concerned [475]. There are, however, two important considerations to which preliminary reference must be made.

The first was emphasized by Warburg nearly twenty years ago in connection with the photolysis of potassium nitrate [496], i.e. that the presence of surrounding molecules is likely to alter very markedly the initial excitation process, so that disturbing forces become operative even while the absorbent molecule is receiving

energy from the radiation. This is, of course, the analogue of pressure broadening in the gas phase, and like it, tends to a certain degree to inhibit the excitation of molecules to levels requisite for reaction, especially if there is a fairly sharp resonance to be considered. If this "field effect" contains any important factors involving impacts between the optically excited molecule and its neighbours, no very clear distinction can be drawn between it and the second of the difficulties to be considered, i.e. collisional deactivation of the excited body in processes not necessarily involving chemical reaction.

An analysis of "absorption distortion" is beyond the scope of this work, but it may be mentioned that such does not always constitute a serious hindrance to straightforward reaction, since both liquid and gaseous hydrogen iodide appear to undergo photochemical decomposition in much the same fashion, and with the same quantum efficiency of ca. 2 [479, 480]. In general, the spectra of both fluorescent and absorbent liquids show the usual band characteristics, except that the rotational fine structure is largely suppressed, in part owing to inner Stark effects induced by the fields of surrounding molecules, and in part due to the smallness of the quantum jumps taking place in complex molecules with large moments of inertia.

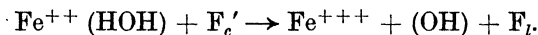
Considering the intensity of the fluorescence exhibited by many substances, it is clear that neighbouring bodies must exert only a very small influence upon the ability of a molecule, such as eosin, to radiate. Any energy transfer in a collision of the second kind must involve practically perfect resonance, so that there is an extremely high probability that a quantum, once emitted, will eventually escape. Some substances can, however, exert a profound extinguishing effect upon the fluorescence, and an admirable research by West, Muller, and Jette [494] has led to the conclusion that no very great difference exists between quenching in the gas phase and in solution. Using an accurate photoelectric method for measuring the intensity of the fluorescence, they find, for example, that the chlorides of lithium, sodium, potassium, rubidium, and lanthanum, in equal concentrations, have exactly the same quenching effect upon the fluorescence of a dilute solution of quinine bisulphate. This would clearly suggest that the negative ions are the active agents, and a more extended study shows that in general the ions lie in the order: $\text{I}^- > \text{CNS}^- > \text{Br}^- > \text{Cl}^- > (\text{C}_2\text{O}_4)^- > \text{Ac}^- > \text{SO}_4^- > \text{NO}_3^- > \text{F}^-$, which is the sequence wherein they fall

as regards deformability, measured from the Rydberg constants to their spectral terms, and from molecular refraction and dispersion data. The natural interpretation is thus, that the energy received by the ion in a collision of the second kind with the photoexcited molecule, goes into inducing a distortion of the electron shell, a process in many ways analogous with excitation. Some exceptions to this rule are occasionally observed, e.g. that KNO_3 , which is practically without action upon quinine sulphate, has a strong quenching effect towards β -naphthol or 1 : 4 naphthalene disulphonic acid, whereas these same substances are indifferent towards KCl present in concentration even up to 4N. It is suggested that this may be due to a shielding of the fluorophoric group by some kind of steric hindrance [cf. 497]. The authors show quite convincingly that the quenching cannot be attributed to other causes such as alterations in the thermodynamic "activities," and it is not necessary to emphasize that their explanation is in harmony with that accepted for many other examples of energy interchange through the medium of collisions of the second kind.

A further investigation upon the photolysis of oxalic acid in the presence of uranyl ions, showed that the fluorescence decreases to a constant minimum, too small to be measured, as the acid concentration is increased, and that at this minimum, where the ratio : $[\text{H}_2\text{C}_2\text{O}_4]/[\text{UO}_2^{--}]$ is unity, then $\gamma = 1$, remaining constant as the proportion of acid is further enhanced. Reaction is hindered by ions which possess an ability to extinguish the fluorescence of the uranyl salt. The photoexcited uranyl ion is thus behaving exactly as the mercury atom in a Cario-Franck experiment, and it is easy to see that with increasing concentration of the complementary substance, the quantum efficiency will approach unity ; the additional fact that this point is reached when $[\text{H}_2\text{C}_2\text{O}_4]/[\text{UO}_2^{--}] = 1$, is, however, suggestive that some loosely bound ion-acid complex is formed, not necessarily as a photochemical process. The extinction of fluorescence in dyes solutions has recently been discussed by Franck and Levi [491] in terms of potential-energy curves, and it appears that the quenching ions can certainly act as the earlier workers suggested.

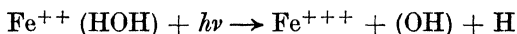
An interesting extension of these views is provided by experiments due to Weber [495] and Weiss [492]. When dyestuffs such as Methylene Blue, Thionine, Cresyl Blue, etc., are irradiated by the full light from a carbon arc in the presence of acidified ferrous sulphate, oxygen being excluded, the solutions bleach and ferric

ions can be detected. If the pH be adjusted ($> ca. 7$) to allow precipitation of the ferric ions, then the bleaching persists, but if they are allowed to remain in the system, the colour of the solution is rapidly regained when the light is shut off. This would suggest, according to Weiss [492], that the hydration energy of the ferrous ions, and the binding energy between the dyestuff and its most loosely bound hydrogen atom, removal of which gives the leucobase, may add on to the energy of the photoexcited dye to give a process :



where F_c and F_l are respectively the coloured and leuco-forms.

The reaction is thus the sensitized counterpart of the direct oxidation :



which has also been observed by Weiss.

A brief theoretical treatment of this mechanism has been given by Weiss and Fischgold [493], who conclude, from an application of Gurney's equations for the passage of an electron through a potential barrier, that the equilibrium constants for these reactions should be derivable from the known potentials of the ferro-ferri and leucobase-dyestuff electrodes. They also postulate, as a necessary consequence of their theory, that effective quenching will be obtained only by the use of substances which can easily lose an electron and be oxidized, while the corresponding criterion for ability to fluoresce must be a similar readiness to acquire an electron. This would seem a dangerously sweeping generalization, and must be treated with reserve until further experimental data are available. Very probably a better explanation will be forthcoming from an application of standard potential-curve theory as developed by Olson [496], which has proved very successful, up to a point, in its use for reactions such as the isomerization of fumaric acid, etc. Discussion of this is, however, beyond the scope of this work, and those desiring information are referred to the Bibliography [497, 498].

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